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ENCYCLOPÆDIA OF CHEMISTRY.

ENCYCLOPÆDIA

OF

CHEMISTRY

THEORETICAL, PRACTICAL, AND ANALYTICAL

AS APPLIED TO

THE ARTS AND MANUFACTURES.

BY WRITERS OF EMINENCE.

ILLUSTRATED WITH NUMEROUS WOOD-CUTS AND STEEL-PLATE ENGRAVINGS.

VOL. II.

GLASS——ZINC.

PHILADELPHIA:
J. B. LIPPINCOTT & CO.
1879.

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CHEMISTRY,

THEORETICAL, PRACTICAL, AND ANALYTICAL,

AS APPLIED TO THE

ARTS AND MANUFACTURES.

GLASS.

GELATIN.—See GLUE.

GLASS.—The transparent compound distinguished by this name is produced by the fusion of silicic salts of the alkaline and earth metals. The etymology of the word has been much disputed. It is derived by some from the Latin *glacies*, ice, its resemblance to which is thought to have suggested the title; and *glacies* may be a contraction for *gelacies*, from *gelu*, frost. Others have remarked that the common Latin designation of this substance is *vitrum;* and as the Romans applied this term, in common with the word *glastum*, to the plant which is now called woad, they have deduced it from the latter of these, either because the ashes of this plant were used in the manufacture of glass, or because it exhibited something of the bluish tinge which is procured from woad. *Glassum*, the name given to amber by the ancient Gauls and Britons, has also been assigned as the origin of the word. But none of these etymons appears very satisfactory. The most plausible theory is that which derives the term from the Saxon verb *glis-nian*, or the German *gleissen*, which are probably contractions of the Anglo-Saxon *gel-ixan*, to shine, to be bright. This view is in a great degree confirmed by the sense in which the term glass and its derivatives are employed by our older writers, who frequently apply it to shining or glittering substances, without reference to colour or transparency.

Glass is a mixture of potassium or sodium silicate, or of both, with one or more silicates insoluble in water—such as the silicates of barium, strontium, calcium, magnesium, aluminium, manganese, iron, or lead. Potassium or sodium silicate (water glass), or a mixture of the two, even with a sufficient quantity of silica to form a very infusible glass, would still be affected by water and acids. Calcium silicate is likewise acted on by acids, but a mixture of it with sodium or potassium silicate resists their action.

Such mixtures of silicate of soda or potash with silicate of lime, &c., are more fusible than the simple salts, and require a smaller amount of silica to render them capable of resisting the action of water and of acids. They contain between 2 and 3 atoms of silica to 1 atom of the metal, and still less when alumina is also present.

The larger the proportion of silica and alumina a glass contains, the more infusible does it become, and the greater resistance does it offer to the action of acids and alkalies. But the greater the excess of potassium, sodium, barium, calcium, magnesium, or lead which it contains, the more easily is it fused and attacked by water, acids, and alkalies. According to BAUDRIMONT and PELOUZE, the lustre and refractive power of glass increase with the atomic weight of the metals contained in it; thus these qualities are possessed in the highest degree by lead glass, next by baryta glass, next by potash glass, and least of all by soda glass (GMELIN, vol. iii.).

In the most remote ages the art of blowing glass into bottles, making it into vases, tinging it to imitate precious stones, melting it in huge masses to make pillars, rolling and polishing it into mirrors, and staining it in parts, were all perfectly known. In all probability Egypt, the parent of so many collateral arts, is to be looked to as its source.

If PLINY is to be credited—an author whose version of the subject has so often been reproduced with all the gravity of history—the discovery of glass was made by some Phœnician soda merchants, who, having landed on the banks of the river Belus, served themselves with blocks of soda to support the vessel in which they prepared their food, and

these masses melting with the heat, transformed into glass the sand on which they rested. Considering the temperature necessary for the making of glass, this story may be rejected as fabulous. Chance had doubtless its share in the invention of glass; but the pottery manufacture and the extraction of metals require the employment of high and sustained temperatures, sufficient to give rise to fusible silicates, more or less analogous to glass. It is a point, however, on which there can be no doubt, that glass was known to the Phœnicians, who for a long time retained the monopoly of it, being favoured by the union of natron, sand, and fuel, in a country situated on the shores of the sea.

There are several references to glass in the Bible. Ballantyne remarks that the Hebrews must have become acquainted with glass while in Egypt, and in consequence of their proximity to the Phœnicians; and it is now generally believed that these two nations had the merit of originating and establishing its manufacture. It is a remarkable circumstance that glass lenses have been found during the recent researches in the ruins of Nineveh. The Egyptians are known to have made enamels of divers hues which they applied on pottery, magnificent specimens of which are still extant, and are called Egyptian porcelain. These are chiefly covered with a beautiful blue or green tinge, and groups of flowers or other designs are traced in black. Glass beads and other ornaments, skilfully manufactured and beautifully tinged, have been found with mummies known to be upwards of three thousand years old. It is certain that Tyre, Sidon, and Alexandria were long celebrated for their glass. To these places the art was exclusively confined for some centuries, and glass was used as an article of luxury, being chiefly in the form of urns or drinking cups of the most elaborate workmanship, and exquisitely embellished with raised, chased, or ornamented figures. The Barberini or Portland vase, composed of a deep azure glass, with figures of a delicate white opaque substance raised in relief, is a splendid specimen which was found in the tomb of Alexander Severus.

Sir J. G. Wilkinson adduces distinct proofs that the art of glass-working was known in Egypt before the exodus of the children of Israel from that land, three thousand five hundred years ago. At Beni Hassan and the Thebes are paintings representing, in a very rude form, glass-blowers at work; and from the hieroglyphics accompanying them, it is found that they were executed in the reign of a monarch who occupied the throne at about that period.

In the reign of Tiberius a company of glass manufacturers established themselves in Rome, and they had a street assigned them near the Porta Capena. The articles of their manufacture were few in number and of inferior quality; neither did they make rapid improvements in their art, notwithstanding the large prices which were then given for glass of foreign manufacture in the imperial city. In the year 220 they had increased so much in importance, and the product was so considerable, that an impost was laid on it by Alexander Severus.

The precise period at which the making of window-glass was introduced is not known. Roman windows were filled with a semi-transparent substance called *lapis specularis*, a fossil of the class of talcs, which readily splits into thin smooth laminæ or plates. This substance is found in masses of 10 or 12 inches in breadth, and 3 in thickness; and when sliced very much resembles horn, instead of which it is to this day often employed by lantern-makers. The Romans were chiefly supplied with this article from the island of Cyprus, where it abounds. So good a substitute for glass it is said to have been, that besides being employed for the admission of light, it was also used in the construction of hothouses, for raising and protecting delicate plants; so that by using it the Emperor Tiberius had cucumbers at his table throughout the whole year.

There is no positive mention of the use of glass for windows before the time of Lactantius, at the close of the third century. But the passage in that writer which records the fact, also shows that the *lapis specularis* still retained its place. Recent discoveries have, however, been made of glazed windows in Pompeii (destroyed A.D. 79). Glass windows are distinctly mentioned by Jerome as being in use in his time. A century later the windows of the church of St. Sophia at Constantinople are represented, by Paulus Silentiarius, as being filled with glass. After this period frequent mention is made of them. Joannes Phillipinus states that glass was fastened into the windows with plaster.

Bede asserts that glass windows were first introduced into England in the year 674, by the Abbot Benedict, who brought over artificers skilled in the art of making window-glass, to glaze the church and monastery of Wearmouth. Other authorities attribute the introduction of this luxury to Bishop Wilfred, junior, who died in 711. It would thus appear that glass windows were first seen in England either about the seventh or the beginning of the eighth century. The use of window-glass, however, was then, and for many centuries afterwards, confined entirely to buildings appropriated to religious purposes; in the fourteenth century it was so much in demand, though still confined to sacred edifices and ornamental purposes, that glazing had become a regular trade. This appears from a contract entered into by the authorities of York Cathedral in 1338, with a glazier, to glaze the west windows of that structure; a piece of work which he undertook to perform at the rate of sixpence per foot for white glass, and one shilling per foot for coloured. Glass windows, however, did not become common in England till the close of the twelfth century. Until this period they were rarely to be found in private houses, and were deemed a great luxury, and a token of great magnificence. The windows of the houses were, till then, filled with oiled paper or wooden lattices. In cathedrals these, and sheets of linen, supplied the place of glass till the eighth century; in meaner edifices lattices continued in use till the eighteenth.

The glass of the Venetians was superior to any

made elsewhere, and for many years commanded the market of nearly all Europe. Their most extensive glass-works were established at Murano, a small village in the vicinity of Venice; but the produce was always recognised as Venetian glass.

The skill of the Venetians in glass-making was especially remarkable in the excellence of their mirrors. Beckmann, who has minutely investigated the subject, is of opinion that the manufacture of glass mirrors certainly was attempted, but not with complete success, in Sidon, at a very early period; but that they fell into disuse, and were almost forgotten until the thirteenth century. Previously to this period plates of polished metal were used at the toilette; and in the rudeness of the first ideas which suggested the substitution of glass, the plates were made of a deep black colour to imitate them. Black foil even was laid behind them to increase their opacity. The metal mirrors, however, remained in use long after the introduction of their fragile rivals; but at length they wholly disappeared, a result effected chiefly by the skill of the Venetians, who by silvering the glass greatly improved the manufacture.

From Italy the art of glass-making found its way into France, where an attempt was made to rival the Venetians in the manufacture of mirrors. The first essay was unsuccessful; but another, made under the patronage of Colbert, had better fortune. A few years afterwards, a discovery or rather improvement in the art of glass-making was effected by Abraham Thevart. This improvement consisted in casting plates of much larger dimensions than it had hitherto been deemed possible to do. Thevart's first plates were cast at Paris, and astonished every artist by their magnitude. They were 84 inches long and 50 inches wide, whereas none previously made exceeded 45 or 50 inches in length.

Early in the fourteenth century the French government made a concession in favour of glass-making, by decreeing, that not only should no derogation from nobility follow the practice of the art, but that none, save gentlemen or the sons of noblemen, should venture to engage in any of its branches, even as working artisans.

The first mention of English window glass is in a contract dated 1439, between the Countess of Warwick and John Prudde of Westminster, glazier, whom she employed to embellish a tomb for the earl, her husband. John Prudde is thereby bound to use no glass of England, but glass from beyond seas. The finest sort of window-glass was first made at Crutched Friars, London, in 1557. The first flint-glass made in England was manufactured at the Savoy House, in the Strand; and the first plate-glass, for looking-glasses, coach windows, and similar purposes, was manufactured at Lambeth by Venetian workmen, brought over in 1670 by the Duke of Buckingham. From that period the English glass manufactories, aided by the liberal bounties granted them in cash upon glass sold for export, became powerful and successful rivals of the Venetian and French manufactories. The bounty on glass exported, which the government paid to the manufacturer, was not derived from any tax by impost or excise previously laid on the raw materials; for all such were returned to the manufacturer, together with the bounty, thereby lessening the actual cost of the article from 25 to 50 per cent., and enabling the English exporter to compete successfully in foreign markets. This bounty provision was annulled during the premiership of Sir Robert Peel, together with all the excise duty on home consumption.

The art of glass-making was introduced into Scotland in the reign of James VI. An exclusive right to manufacture it within the kingdom, for the space of thirty-one years, was granted to Lord George Hay in the year 1618. This right his lordship transferred in 1627, for a considerable sum, to Thomas Robinson, merchant-tailor in London, who again disposed of it for £250 to Sir Robert Mansell, vice-admiral of England. The first manufactory of glass in Scotland, an extremely rude one, was established at Wemyss, in Fife. Regular works were afterwards commenced at Prestonpans, Leith, and Dumbarton.

Composition of Glass.—This substance is the product of fusion at a high temperature of the metals of the alkalies and alkaline earths, or silicic acid, sometimes of boracic acid, with lead, tin, iron, manganese, &c. The product solidifies after fusion in the form of a transparent mass, which is either colourless or not, according to the ingredients which it contains; it combines a great degree of hardness with the property of resisting the destructive action of air, water to a certain extent, and even that of the more powerful chemical agents. It is well known that silica acts the part of a powerful acid at the temperature of a red heat, and is capable of expelling carbonic acid, hydrochloric acid, &c.

Those varieties of glass which possess the highest degree of lustre and power of refraction are also the softest, that is, the most easily scratched. They are likewise those which exhibit the highest specific gravity (from 2·8 to 3·6) and, as might be deduced from that circumstance, they (at least as far as the colourless glasses are concerned) are those which contain bases with a very high atomic weight—oxide of lead, baryta. Those bases, on the contrary, which render the glass hard and durable, appear to produce little lustre or power of refraction. The specific gravity of these varieties lies between 2·37 and 2·56.

There is much difficulty in dividing the glasses according to any definite principle. One of the simplest arrangements is given by Tomlinson, as follows:—

1. Silicate of potash and oxide of lead. Examples:—*Flint-glass*, *crystal*, and *strass*.

2. Silicate of soda and lime; or silicate of potash, soda, and lime. Examples:—*Common window*, *English crown*, and *plate*.

3. Silicate of potash and lime. Examples:—*Foreign crown*, *refractory Bohemian glass*.

4. Silicate of soda, lime, alumina, and oxide of iron. Example:—*Coarse green wine-bottle glass*.

Bottle-glass, or what is more properly described by the German term *Hohlglase*, or *Hollow glass*, com-

prises all glass worked into the form of vessels or tubes. According to the purity of the "metal," which is the technical term given to glass in the fused state, this variety is subdivided into different qualities, such as —*Ordinary bottle-glass*, consisting of silica, potash or soda, lime, alumina, and oxide of iron; *glass used for medicinal bottles*, consisting of silica, soda, lime, some alumina, and a very little ferrous oxide; *white bottle-glass* for bottles or phials, tumblers, tubes—containing silica, soda or potash, and lime.

Window-glass, including *English crown* and *cylinder* or *sheet-glass:* this is a silicate of potash or soda, lime, and alumina.

Plate-glass, composed of silica, soda or potash, lime, and a little alumina. This variety only differs from the preceding by the greater purity and freedom from colour of the materials.

Flint-glass, used for grinding, &c., composed of silica, potash, and oxide of lead.

Crystal, for optical purposes and table-ware, consists of silica or silicic acid, and potash, with more lead than the preceding. In short, it is a simple flint-glass, formed with very pure materials.

Strass, or the substance composing the imitation of precious stones, known as paste, consists of silica and potash, with a still larger amount of oxide of lead: it is coloured by various materials.

Enamel, a silicate and stannate or antimoniate of potash or soda, and of oxide of lead. It may be otherwise described as composed of silica, soda or potash, and oxide of lead—rendered opaque by oxide of tin or antimony.

Soluble Glass, which is a simple silicate of potash or of soda, or a mixture of these two silicates.

ANCIENT GLASS.

	Analyst.	SiO_2.	Na_2O.	K_2O.	CaO.	MgO.	MnO.	PbO.	Fe_2O_3.	Al_2O_3.	SO_3.
Egyptian glass rod, colourless,.....	Benrath.	72·30	20·83	—	5·17	—	—	—	0·51	1·19	—
" small block, grass green,..	"	70·58	20·70	—	6·54	—	trace.	—	0·99	1·19	—
" " tinged with green,	"	71·15	18·76	—	8·56	trace.	0·44	—	0·25	0·84	—
Roman flask (Treves),.....	"	70·66	17·47	—	8·38	—	—	—	1·24	2·25	—
" bottle, greenish (Treves)....	"	68·10	20·53	—	6·51	0·49	1·93	—	1·09	1·30	—
" " green (Kreuznach),..	"	67·96	22·39	—	5·12	trace.	1·67	—	0·69	1·86	0·32
" urn, blue-green (Wolfsheim),	"	70·32	21·95	—	3·04	0·29	0·87	—	1·92	1·61	—
" fragment of handle, blue-green (Panticapalum).....	"	72·11	15·46	—	7·52	—	0 56	—	1·02	2·95	0·38
" lachrymatory (Panticapalum),	"	69·55	16 01	—	8·43	—	2·32	—	1·48	2·21	—
" bottle-neck, grass green (Panticapalum),.....	"	67·10	18·67	—	8·05	1·16	trace.	—	1·73	3·29	—
Egyptian rod, brown,.....	Schuler.	65·90	22·33	—	8·42	—	0·94	—	0 97	1·44	—
Roman urn (Puzzuoli),.....	"	70·58	18·86	—	8·00	trace.	0 48	—	0·53	1·80	—
" lachrymatory (Puzzuoli),....	"	71·45	16·62	—	8·14	trace.	0·17	—	1·02	2·25	—
" fragment (Pompeii),.....	Claudet.	69·43	17·31	—	7·24	—	0·39	—	1·15	3·55	—
" from grave,.....	Siegwart.	64·25	23·22		7·54	1·44	—	—	3·52		P_2O_5.
Jerusalem, glass from the temple,..	D. Campbell	69·30	13·79	1·49	8·50	0·55	—	trace.	2·00	3·30	0·80

MODERN GLASS—WHITE SODA GLASS.

	Analyst.	SiO_2.	Na_2O.	CaO.	MgO.	MnO.	ZnO.	Fe_2O_3.	Al_2O_3	F.
Window glass, French,.....	Dumas.	69·65	15·22	13 31	—	—	—	—	1·82	—
" " "	"	69·25	11·30	17·25	—	—	—	—	2·20	—
" " "	"	68·55	12·88	16·17	—	—	—	—	2·40	—
" " "	"	68·65	17·70	9·65	—	—	—	—	4·00	—
" " "	"	68·50	13·70	7·80	—	—	—	—	10 00	—
" " "	"	68·00	10·10	14·30	—	—	—	—	7·60	—
" " English,.....	"	69·00	11·10	12·50	—	—	—	—	7·40	—
" " "	Richardson.	66·..7	14·23	11·86	—	—	—	—	8·16	—
" " Chance, Birmingham,....	Cowper.	71·40	15·00	12·40	—	—	—	—	0·60	—
Plate-glass, French,.....	Berthier.	72·00	17 00	6 40	—	—	—	1·90	2 60	—
" "	Tassaers.	76·00	17·00	6·00	—	—	—	1·00	—	—
" "	Dumas.	75·90	17·50	3·80	—	—	—	—	2·80	—
" German,.....	Jaeckel.	72·31	11·42	14·96	—	—	—	—	0·81	—
" St. Gobain,.....	Peligot.	73·00	11·50	15·50	—	—	—	—	—	—
Sodium glass, "	Pelouze.	77·04	15·51	7·41	—	—	—	—	—	—
Sulphate of soda glass, St. Gobain,.....	"	73·05	11·79	15·16	—	—	—	—	—	—
Plate-glass, Munster,.....	Benrath.	72·12	12·23	14·82	—	—	—	0·50		—
" "	"	71·56	12·97	13·27	—	—	—	1·29		—
" Charleroi,.....	"	73·31	13·00	13·34	—	—	—	0·83		—
" Chance, Birmingham,.....	"	70·71	13·25	13·38	—	—	—	1·92		—
" " 2nd. quality,.....	"	72·90	12·45	13 26	—	—	—	1·93		—
" Munster, "	"	78·72	12·92	6 51	—	—	—	1·65		—
Window glass, St. Petersburgh,.....	"	71·27	20·10	8·14	—	—	—	1·98		—
Best white French glass,.....	Pelouze.	72·10	12·40	15·50	—	—	—	—	—	—
" " "	"	77·30	16·30	6·40	—	—	—	—	—	—
White bottle glass, Bavarian, ...	Benrath.	78·39	13·91	7·10	—	—	—	0·60		—
" " Russian,.....	"	74·71	15·74	8·77	—	—	—	0·78		—
" " French,.....	Berthier.	72·00	17·00	6·50	—	—	—	4·50		—
" " "	"	76·00	16·00	7·00	—	—	—	1·00		—
Cryolite glass, United States,.....	Benrath.	67·07	19·83	trace.	—	1·09	—	1·02	10·99	—
" " "	Williams.	63·84	10·51	1·86	0·25	1·12	6·99	1·50	7·86	8·05
" " "	"	63·40	5·85	—	—	—	6·50	1·40	3·67	—

WHITE POTASH GLASS.

	Analyst.	SiO_2.	Na_2O.	K_2O.	CaO.	MgO.	MnO.	Fe_2O_3.	Al_2O_3.
Plate-glass, French,	Dumas.	73·80	12·10	5·50	5·60	—	—	—	3·50
" Venetian,	Berthier.	68 60	8·10	6·90	11·00	2·10	0·10	0·20	1·20
" Bohemian,	Peligot.	67·70	—	21·00	9·90	—	—	—	1·40
" "	"	76·00	—	15·00	8·00	—	—	—	1·00
" British Plate-glass Co., St. Helens,	Mayer & Brazier.	77·36	13·06	3·01	5·31	—	—	0·91	trace.
" London Thames Plate-glass Co.,	" "	78·68	11·63	1·34	6·09	—	—	trace.	2·68
" London and Manchester Plate-glass Co., St. Helens,	" "	77·90	12·35	1·72	4·85	—	trace.	—	3·59
" Hanoverian,	Emmerling.	73·79	13·94	0·60	8·61	0·12	0·32	0·68	0·58
" "	"	72·69	12·83	1·77	9·20	0·34	0·54	0 97	0·63
Bohemian tubes,	Rowney.	73·13	3·07	11·49	10 43	0·26	0·46	0·13	0·30
" "	Otto.	74·40	—	18·50	7·20	—	—	—	0·10
" drinking glasses,	Berthier.	71·70	2·50	12·70	10·30	—	0·20	0·30	0·40
" "	Gros.	71·60	—	11·00	10·00	2·30	0·20	3·90	2·20
" common glass,	Dumas.	69·40	—	11·80	9·20	—	—	—	9·60
French tubes,	Berthier.	69·20	3·00	15·80	7 60	2·00	—	0·50	1·20
" crown glass,	Dumas.	62·80	—	22·10	12·50	—	—	2·60	

LEAD GLASS.

	Analyst.	SiO_2.	Na_2O.	K_2O.	CaO.	ZnO.	PbO.	Fe_2O_3.	Al_2O_3.
English crystal,	Faraday.	51·93	—	13·67	—	—	33·28	—	—
" " London,	Berthier.	59·20	—	9·00	—	—	28·20	0·40	—
" " "	Salvétat.	57·50	1·00	9·00	—	—	32·50	—	—
" " Newcastle,	Berthier.	51·40	—	9·40	—	—	37·40	0·80	1·20
French crystal,	Sauerwein.	48·10	—	12·50	0 60	—	38·00	0·50	—
" "	Salvetat.	61·00	—	6 00	—	—	33·00	—	—
" "	"	51·00	1·70	7·60	—	—	38·30	1·30	
" "	"	54·20	0·90	9·20	—	—	34·60	0·50	
" "	Benrath.	50·18	—	11·62	—	—	38·11	0·04	
Flint glass,	Faraday.	44·30	—	11·75	—	—	43·05	—	—
"	Dumas.	42·50	—	11·70	0·50	—	43·50	—	1·80
Crown glass, Maes,	Schüler.	56·61	24·68		0·70	13·49	4·11	0 40	

BOTTLE GLASS.

	Analyst.	SiO_2.	Na_2O.	K_2O.	CaO.	MgO.	MnO.	Fe_2O_3.	Al_2O_3.
French, Sauvigny,	Berthier.	60 00	3·10		22·30	—	1·20	4·00	8·00
" St. Etienne,	"	60 40	3 20		20·70	0·60	—	3·80	10·40
" Epinac,	"	59·60	—	3·20	18·00	7·00	0·40	4·40	6·80
" Sevres,	Dumas.	53·55	—	5·48	29·22	—	—	5·74	6·01
" Clichy,	"	45 60	—	6·10	28·10	—	—	6·20	14·00
Bohemian Champagne bottles,	Maumené.	58·40	9·90	1·80	18·60	—	—	8·90	2·10
" "	"	62·21	5·69	1·91	22·93	—	—	6·10	1·16
" "	"	63 34	4·17	2·01	21·34	—	—	4·42	4·72
German,	Benrath.	69·82	18·28	1·50	7·82	—	—	2·58	
"	"	62·78	19·14	11·24	6·11	—	—	0·73	
"	"	64·41	15·76	10·50	5·81	—	—	3·52	
Russian,	"	65·77	11·75		16·58	—	—	5·90	
"	"	68·38	19·03		10·19	—	—	2·40	

Chemical Constitution of the Different Glasses.—From a careful inspection of the preceding tables, it will be seen that the constituents of the different varieties of glass are chemically combined. It follows that the individual constituents must be united in equivalent proportions, though these relations are sometimes difficult to trace, in consequence of different metals replacing each other.

The varieties of soda glass correspond approximately to the formulæ.

	Soda.	Lime.	Silica.
$Na_2O.CaO.6SiO_2$	13·0	11·7	75·3
$5Na_2O.7CaO.36SiO_2$	10 8	13·7	75·5
$5Na_2O.6CaO_233SiO_2$	11·8	12·8	75·4

Potash glass to the formulæ:—

	Potash.	Lime.	Silica.
$K_2O.CaO.6SiO_2$	18·5	10·9	70·6
$5K_2O.7CaO.36SiO_2$	15·6	12·9	71·5
$5K_2O.6CaO.33SiO_2$	16·9	12·0	71·1

And lead glass to:—

	Potash.	Lead oxide.	Silica.
$K_2O.PbO.6SiO_2$	13 9	32·9	53·2
$5K_2O.7PbO.36SiO_2$	11·2	37·2	51·6
$5K_2O6PbO.33SiO_2$	12·4	35·3	52·3

Comparative Fusibility of the Glasses.—Under the influence of a cherry-red heat and upwards, all kinds of glass are capable of being first softened and then undergoing a complete fusion. At the same time, the difficult fusibility of those varieties in which silicic acid preponderates, are very important facts in connection with the manufacture of glass. Silicic acid *per se* is perfectly infusible, but it acquires the property of fusibility in a greater or lesser degree, according to the quantity of metallic oxide with which it is mixed. Glass-makers, in short, call all the bases *fluxes*, and are well aware that the work is facilitated and fuel saved by increasing the amount

of flux in the mixture; but, at the same time, they know that the addition of flux cannot exceed a certain limit without detriment to the durability of glass. When glass is attacked by reagents, under ordinary circumstances, a removal of the metal always results. Glasses containing lead are the most fusible, and the more so in proportion as they contain a more considerable quantity of oxide of lead. Common glasses, on the contrary, are less so the more lime and alumina they hold. Thus, flint-glass and crystal are more fusible than common-glass, and the latter is a little more so than bottle-glass.

Imperfect Fluidity of Glass.—The possibility of casting or moulding glass, as well as its purification, depends upon the fact that at very intense heats the so-called *metal* is tolerably fluid, though still possessing a consistence which may be compared to that of weak syrup. In this state the heavier impurities are enabled to subside to the bottom, while the bubbles of gas, which too often form flaws in glass, rise by their levity to the surface. At a brisk red heat, on the contrary, the metal is only in a semi-fluid state, and on this peculiar and valuable property depends the possibility of working it into every variety of form. In this state it is an exceedingly tough, thick mass, possessing great ductility, and capable of being drawn out into the finest threads, or blown into the form of the thinnest hollow spheres.

Brittleness.—When glass has been heated to the softening point, and exposed to a rapid cooling, it is very brittle; when, on the contrary, it is submitted to a slow cooling, it becomes capable of resisting pretty severe shocks without breaking, and it stands equally well sudden variations of temperature. The metamorphosis has been attributed to unequal crystallization. It will be seen afterwards that the particles of glass always exhibit in the fluid state a tendency to arrange themselves in a regular manner, and form crystals. Now, when the mass is allowed to cool suddenly, no time is allowed the particles to follow this tendency, and they are forced, as it were, against their inclination to remain in that relative position towards each other which they assume during the working, or in other words, to form an amorphous mass. This forced relative position of the particles is greatest where the glass has been rapidly cooled; the interior of the mass is, therefore, not so subject to it as the surface, and this latter also contracts in a greater degree. The outer layers are, consequently, in a state of tension, with reference to those in the interior. It is obvious, therefore, that there must be a want of uniformity in the attractions of the particles of glass for each other; that a tendency to subvert the force of cohesion has been induced, which the slightest impulse from without will be sufficient to call into action. This circumstance perfectly explains the brittle nature of glass, which sometimes rises to a very extraordinary degree. For example, if one takes a little melted glass, and allows it to fall, drop by drop, into cold water, each drop will suddenly solidify, and will take a form generally spheroidal or ovoidal, terminated by a tail which ends in a rapidly tapering point, *a*, as represented in Fig. 1. The surface of the globular part of this drop of glass is harder than ordinary. But by merely

Fig. 1.



breaking off the point, *a*, the tension is called into play, and the whole mass flies in pieces, or rather is instantly converted into a fine powder with a slight detonation. This observation was made by Prince Rupert, and the glass tears thus treated are known as *Rupert's drops.*

The effect is explained by Dumas, by supposing that by the immersion in cold water the surface of the glass is suddenly solidified, the central parts being still fire-red, and consequently much dilated. When these last become solidified and cooled down, they must have retained points of adherence to the surface, and consequently occupy a larger volume than that which agrees with the temperature to which they are reduced; the central molecules are, therefore, more distended than usual, and exert a powerful contracting force on the surrounding parts. At the instant when a part of the envelope or outer portion is broken, the molecules which had been retained by it briskly contract, draw in with them all the others, and thus determine a multitude of points of rupture; as this effect is instantaneous, each fragment is shot with force, and drives the air before it; this fluid, therefore, undergoes a sudden dilatation and contraction, from which results the detonation that is heard.

The same effect is produced under another form, in what is termed the *Bologna* or *philosophical phial*—Fig. 2. This is a kind of short tube, thick, and closed at one end, which is obtained at crystal manufactories, by blowing a small portion of glass to judge of the state of the metal in the pots during the melting. These tubes are very thick, for they must be sufficiently so to allow of appreciating exactly the tint of the glass. They are exposed to a rapid cooling, because the object which they are intended to serve does not require that any care should be taken in that respect. This cooling is even accelerated by shaking in the air the rod which supports the small tube. The latter is then, in point of fact, in a state very analogous to that of the Rupert drops, and Dumas explains their remarkable brittleness in the same manner. The interior parts have undergone a slow, and the exterior parts, on the contrary, a rapid cooling; and when these tubes are struck, even very strongly, on the outside, they do not break, while the slightest stroke on the inside by a sharp edged substance is sufficient to make them fly in pieces, with a detonation similar to that which occurs in the case of the Rupert drops. Moreover, they resist the blow of a marble or bullet let fall from a distance of 3 or 4 feet into the interior of the tube, whilst a small fragment of flint, or even a

Fig. 2.



grain of sand, falling from the height of a few inches is sufficient to make them burst asunder.

Phenomena more or less analogous to these happen with any thick glass vessels which have been quickly cooled. By slight variations of temperature, such as occur when they are carried from a room without a fire into a warm room, it sometimes happens that these glasses suddenly burst without any apparent cause. It is obvious that the thicker the glasses, the more readily will effects of this kind be produced. Tubes of glass somewhat thick, and especially those which are of unequal thickness, are also very subject to split, and usually the crack is prolonged through the whole length of the tube. This is because glass tubes are not submitted to that particular operation, the object of which is to render glasses less liable to break by sudden changes of temperature. This operation is termed *annealing*, and consists in submitting the glass to a very slow refrigeration. The details of the process will be described in connection with the general arrangements of the glass-house and its furnaces, among which the annealing arch or oven takes an important place.

It would seem that the ordinary annealing of glass, whether it be that the operation is badly performed, or that it has not a durable effect, always leaves something to be desired. For some articles a method of annealing is employed which is very simple, but at the same time expensive, if required to be applied on a large scale. It consists in placing the glass vessels in a trough or pan, taking the precaution to separate them by a little hay or straw. The vessels and the pan are filled with water, and the liquid is brought to ebullition. The whole is then left to cool slowly. The vessels thus treated are, so to speak, insured against any rapid change of temperature comprised within the interval of 180° Fahr., or thereabouts. By using a bath of water charged with some salt, an oil-bath, or a bath of fusible alloy, this method might be extended to higher temperatures.

The efficacy of the process rests on the great difference which exists between the conducting power of air and that of liquids. There is no doubt that in the operation of annealing in the air, different points of the surface are cooled at different rates, a circumstance which can never occur when the annealing is effected under a liquid mass. It is well known in laboratories, that vessels which have accidentally undergone an annealing of this kind are thereby rendered very fit to support, without breaking, rapid changes of temperature. This suggestion has been very ably worked out by F. B. A. Royer de la Bastie in a process which he terms the "tempering of glass," and which will be fully described further on.

Devitrified or Semi-crystallized Glass.—As excessive brittleness results from the sudden cooling of glass, so, on the other hand, when the fused metal is cooled too slowly, the amorphous state entirely disappears, the mass assumes a crystalline structure, and other changes occur which are termed *devitrification*. If the glass contain different metals a partial separation takes place; the silica divides itself between the metals, and thus forms compounds of definite proportions which crystallize separately. In this case the intimate mixture of the materials which constitute the true glass is destroyed; the glass becomes *very hard, fibrous, opaque, much less fusible, a better conductor of electricity and of heat.* The first glass of this kind was produced and described by Réaumur, and was termed by him *devitrified glass.*

The devitrification of glass is a general phenomenon, which exhibits itself in all kinds of glass, but especially in glass with several earthy bases, and more difficulty in lead glass, or glasses simply alkaline. It is produced by melting the glass, and allowing it to cool very slowly, or else by heating the glass to the softening point, and submitting it to a prolonged heat and a graduated cooling. The operation succeeds better with bottle-glass than any others; then comes common green glass, next white glass, then simple glass. with a soda base; after this, flint-glass, and, lastly, simple glass, with a potash base.

This property exerts a great influence in the manufacture of glass. It explains, indeed, why, in the making of bottles, so much care is taken to avoid the repeated reheating of the mass which is to be formed into that article. It would be thoroughly devitrified in a few seconds; the glass would become hard, difficult to fuse, and would present a multitude of solid grains disseminated in a matter still soft. One sees in the same manner why green glass, and even common white glass, and, still more so, bottle glass, can only be shaped by the lamp of the enameller when the work is performed with great despatch. If he works so slowly that he is obliged to reheat several times the glass tube which he is blowing, the mass devitrifies, and all the phenomena show themselves which have just been described. In vain does he then try to blow a bulb—all the force of his lungs will not avail; the glass is no longer soft. Besides, the material then becomes rugous, semi-opaque, and almost infusible.

One can understand, on the same principle, how important it is to select with care glasses intended to be used in large and thick masses, such as those designed for the making of lenses for large optical instruments. The cooling of such masses is necessarily very slow, which induces the devitrification of the glass. It is almost impossible to succeed, therefore, except with glass containing lead and potash, or potash and lime. Indeed, these two kinds of glass, which constitute *flint* and *foreign crown* glass, are employed exclusively on the Continent for the making of objectives for achromatic telescopes.

The devitrification of glasses is a phenomenon of the greatest interest, and to which the attention of glass-makers should be much directed. It will appear still more worthy of consideration when it is shown that, in virtue of its properties, devitrified glass is capable of replacing porcelain in almost all its uses. Thus, tubes, retorts, receivers, capsules, &c., can be made, which resist the fire as well as vessels of porcelain, which are as impermeable as common glass, which resist acids very well, and which, in fine, may be obtained in a single piece, under a thousand diversified forms, which the moulding of porcelain

could only furnish with difficulty. This is a business yet to be created, which will furnish vessels of a wholesome, elegant ware, and at a comparatively low price. Of late years De la Bastie has manufactured a white opaque glass on this principle.

To effect the devitrification of glass, Réaumur selected common bottle or green glass. He filled the vessels with a mixture of roasted sulphate of lime and white sand, reduced to fine powder. He introduced them into an earthen box, which itself was filled with a similar mixture, taking care that the vessels were well isolated from each other, as well as from the sides of the box, the empty space being occupied with the plaster and sand. The box, thus prepared, fitted with a lid and luted, was carried into a pottery furnace, and left to itself during the whole duration of a firing. At the end of that time the glass was entirely devitrified.

The fracture of this glass is silky; exactly in the middle of its thickness is a brown line, and it is at this point that an infinite number of small crystalline needles meet, proceeding from the exterior and interior surface of the vessel. These needles, perfectly parallel to each other, are perpendicular to the surface of the glass, as well as to the plane passing through the line of junction, which itself follows all the variations of form in the glass. It may be added that in glasses imperfectly devitrified the two surfaces exhibit similar needles, but too short to meet, and, consequently, separated by a greater or less breadth of common glass, which occupies the middle of the thickness of the plate or vessel. It is evident, therefore, that whatever cause determines the crystallization of the glass acts first on the surfaces, and afterwards penetrates to the middle, till the crystals setting out from the two opposite points come to meet.

Devitrification is a crystallization of glass. Experience proves that glass, slowly cooled, almost always crystallizes when the passage from the liquid to the solid state is effected so gently as to allow the requisite molecular arrangements to take place. But it appears that, by applying this idea in an absolute manner to the devitrified glasses of Réaumur, a grave error would be committed. There exist, in fact, two distinct kinds of devitrified or crystallized glasses, resulting from different action. 1. The first class embraces glasses which, by means of a prolonged heat, and sometimes by the aid of a suitable lute or cement, *have arrived at a state of homogeneous combination, and have taken the crystalline form, losing some of their constituent principles.* 2. The second kind comprises glasses which, by means of a solidification very slowly effected, *are divided into two or more different compounds, some of which have preserved the uncrystallized state, while others have taken a regular crystalline form.*

The chemical changes observed in the devitrification of bottle-glass consist:—1st. In the loss of a part or the whole of the potash. 2nd. In the passing of a part or the whole of the ferrous and manganous oxides to the state of ferric and manganic oxides. 3rd. In the formation of one or more definite and crystallized silicates, by means of the remaining products.

The second process of devitrification, which consists in the mass being broken up into different chemical compounds, presents itself sometimes alone, but often simultaneously with the preceding. At the glass-works of Choisy-le-Roi a glass was formed with 100 of sand and 40 of carbonate of soda, perfectly pure and dry. This glass being cooled rapidly, was transparent like ordinary glass. It was re-melted, and submitted to a slow cooling, that the solidification might take place tardily. A glass was thus obtained which was milky, grainy, and evidently devitrified in some places. The devitrified parts were re-melted, and rapidly cooled again after the melting, when they became common glass once more. This glass, by a new fusion and a prolonged cooling, gave a glass better devitrified than it was the first time. Lastly, the portions which exhibited the most perfect devitrification, being again melted and quickly cooled, again yielded a glass endued with its ordinary characteristics.

This remarkable experiment sufficiently proves that, in the slow solidification of glass, a division of its elements is determined, in consequence of which a definite silicate crystallizes, and thus separates from the remaining mass.

In fact, devitrification is a crystallization of glass, due to the formation of definite compounds infusible at the temperature existing at the instant of the devitrification. Sometimes this infusibility is produced by the volatilization of the alkaline base; sometimes by a simple division or separation, the alkali then passing into that portion of the glass which preserves the vitreous state. All glasses may therefore be devitrified, for all glasses are capable of passing to the state of definite, and consequently crystallizable, silicates. Glasses which contain at the same time indifferent oxides and basic oxides will devitrify better than others, by the tendency which the indifferent silicates and basic silicates have to combine in definite proportions. Lastly, devitrified glasses will possess very variable properties, for their composition itself will differ completely, according to the nature of the glasses and the circumstances of the devitrification. Thus, sometimes the devitrified glass will be crystallized in needles of considerable size, as happens with window-glass; sometimes it will be crystallized in very fine needles, or even simply transformed into an opaline mass, without appearance of crystals, as in the case of bottle-glass.

Specific Gravity of Different Kinds of Glass.—It is evident that the specific gravity of glass must depend on its composition. Alkaline calcareous glasses are the lightest; bottle-glass comes next: then plumbiferous glasses. The following are the results of some experiments:—

	Specific Gravity.
Bohemian glass,	2·396
Crown-glass,	2·487
Saint Gobain plate-glass,	2·488
Cherbourg plate-glass,	2·506
Window-glass,	2·642
Bottle-glass,	2·732
Crystal, or common flint-glass,	2·9 to 3·255
Optical flint-glass,	3·3 to 3·6

Muspratt found several kinds of glass to give the following specific gravities:—

White flint-glass,	3·000
Bottle, common green,	2·715
Green glass, St. Helen's,	2 654
Crown-glass,	2·520
Leith crystal,	3·189
Plate-glass,	2·439

Chemical Properties of Glass.—Air or oxygen, cold or hot, provided they are dry, exercise no action on glasses. It is not so with moist air, as will be seen further on, especially with reference to soluble glass. In this case, however, the reagent is water.

Deoxidizing bodies, on the contrary, act with the aid of heat on glasses which contain oxides of iron or of manganese, and especially oxide of lead. In fact, when lead glass is heated with charcoal, or in a current of hydrogen, the oxide of lead is reduced, and the metal being set free, communicates to the glass a blackish tint. This effect is even so rapid that one cannot operate on crystal glass before the blow pipe without blackening it greatly, except particular precautions be used.

Water acts more or less on all glasses; and there is a great number which it tends to decompose into a soluble alkaline silicate, and an insoluble earthy and alkaline silicate. It produces in some sort the same separation which would result from a slow cooling or from the devitrification of the glass.

This decomposition takes place most readily with those glasses which contain much soda or potash, these alkalies being dissolved out by hot water. Bischof remarks that the powder filed from a white glass tube reddens moist turmeric paper. Faraday found that powdered plate-glass acts in a similar way. Window glasses, or those which have an analogous composition, are altered in this manner by boiling water. So much is this the case, that water which is boiled for a long time in glass vessels becomes alkaline and turbid by the portion of earthy and insoluble alkaline silicate which forms the residue of its action, and which, detaching itself from the sides of the vessel, remains in suspension in the liquid. Lastly, these same glasses have almost always so much of a hygrometrical property, as to become covered with a thin coating of water when they are exposed to the contact of moist air. This property should not be lost sight of in choosing glass for electrical purposes.

Looking-glasses sometimes tarnish in the air. This result proceeds from the deposit of a film of hygrometrical water; the same is observed on the glasses of optical instruments. If the glass is well made, the effect proceeds no further; but if it is too alkaline, the deposited water gradually acts upon its surface, and thus produces a decomposition similar to that above mentioned; in this case the glass is tarnished beyond remedy, or at least it must be repolished. Sometimes the tarnishing is scarcely perceptible, and yet a great alteration may have been produced on the surface. This is observed when the glass is heated; its surface becomes detached in very thin lamellar scales, presenting a great regularity of fracture. These scales Griffiths has shown to be silica, and to be identical with the pearly flakes seen on specimens of antique glass which have been long buried. The glass then remains completely deprived of its polish, wrinkly, and almost opaque.

Glass-tubes, globes, retorts, and even measures or standing-glasses which in laboratories are long exposed to moist air, very often exhibit the same phenomena. In this state the tubes, for example, can no longer be heated at the lamp without losing their polish. Watch-glasses are often observed in the same condition, and even the glass of optical instruments. It appears, indeed, that glasses which have been polished are more liable to this effect than common glasses. It is well known that glass which has not been polished presents a harder and more brilliant surface, which seems due to the *tempering* it undergoes at the instant of cooling. It is possible, therefore, that polishing renders glasses more readily attacked, by exposing the interior part of the mass, and destroying the hard coat which secured it.

The windows of houses, offices, or public buildings of an old date, often present a tarnished and unpolished surface, the origin of which must be attributed to a similar cause. When the hygrometrical water has attacked the glass, the slightest changes of temperature cause its surface to splinter, which thus becomes dull, devoid of polish, or at least cracked, and disposed to rise in scales by the least rubbing. This effect may especially be remarked in the windows of stables; these, after some years, are always so much altered as to exhibit all the phenomena of the decomposition of light produced by thin plates. The alteration observed in old glass that is found in ruins or in tombs is very remarkable. Its surface is sometimes entirely decomposed; it has become opaque, and the slightest rubbing causes it to peel off in thin light pellicles, exhibiting all the colours of the rainbow.

Since water *per se* is capable of acting on glass with so much energy, it will readily be conceived that concentrated solutions of potash and soda must be capable of attacking it still more powerfully. Even ammonia attacks many kinds of glass. Griffiths states that a flint glass bottle which had long contained a solution of carbonate of ammonium became so fragile that on shaking it flakes of glass were detached.

At a red heat, not only potash and soda, but all the carbonates and all the bases of that class, combine with the elements of glass to constitute glasses more basic. When carbonate is used, the carbonic acid is expelled. It may even be said that all the oxides not decomposable by heat, when heated with glass, combine with it, and thus form glasses transparent or opaque, coloured or colourless, more or less readily acted on than the glass employed, according to the proportions. In general, when the proportion of oxide added is much increased, the glass is rendered soluble in acids. This is done in the analysis of glass, when it is heated with carbonate of sodium, carbonate of barium, or oxide of lead.

All acids act on glass. Among these hydrofluoric acid must be classed by itself, its action being quite peculiar. From powdered flint-glass hydrochloric acid extracts the potash only; but in distilling it in a green glass retort Hess obtained crystalline silica, while the chloride of potassium and ferric oxide passed into solution. The other acids tend to decompose glass, by seizing on the metals and setting the silica free.

Among the bottle glasses, there are many which resist the action of wine, and which, nevertheless, are powerfully attacked by nitric, hydrochloric, or sulphuric acid. Salts of lime, of iron, of alumina, and alum, are formed when sulphuric acid is used. This acid produces in the interior of the bottles crystalline nipples or pustules, the base of which ultimately pierces the vessel; these pustules are sometimes of the size of a bean; in all cases the silica set free assumes a jelly-like appearance.

A bottle-glass too rich in alumina is one of those which the acids most readily attack. Dumas states that he has seen such glasses, which the bitartrate of potash contained in the wine attacked so quickly that the alteration was perceptible at the end of a few days. The salt of alumina produced discolours the wine, and imparts to it a disagreeable taste. The bottle becomes corroded, and a flaky deposit is detached from it. At the same time, crystals of different salts are deposited.

Glasses containing lead are the more easily acted on in proportion as they are too rich in lead. Well-made crystal resists acids well. It is the same with window glasses; when too alkaline they are acted on very easily; when well made, they resist. Moreover, when a glass loses its polish by heat, one may be sure that it is of a nature to be attacked by acids.

Hydrofluoric acid transforms silica into water and fluoride of silicium, and therefore acts on all glasses. Its action, in fact, would be always quick and complete, if the formation of a certain quantity of double fluoride of silicium and sodium, of potassium, or calcium, or lead—double fluorides which are all insoluble, or only slightly soluble—did not diminish the contact, and consequently the effect produced.

Hydrofluoric acid, however, attacks glass rapidly when the action is exerted on a small surface, and much acid is employed. This property has been turned to account to etch glass; the acid is employed in a gaseous or liquid state, according to the occasion and the end proposed. The gaseous acid produces opaque traces; the liquid acid transparent ones.

Manufacture of Glass.—There are no reliable records of the processes employed by the ancients in the making of glass. But from the time when Agricola described this art, the general arrangement of the furnaces, the mode of fabrication, and the nature of the materials employed, have undergone only modifications of detail, without any change in the general character of the process.

Raw Materials for Glass-making.—The chemical or theoretical composition of the different varieties of glass has been already given; but as it is quite impossible to obtain or prepare the ingredients in a state of chemical purity previous to fusing them together, it will be necessary to explain the sources from which the materials that go to constitute the different glasses are practically derived for the purposes of the manufacture.

Silica.—It has been stated that all true glasses are practically composed of silica, *i.e.*, silicic acid, in combination with at least two alkaline or earth metals, and sometimes with lead, zinc, and other metals. Silica, silicic acid, or silicic oxide (SiO_2) is very abundant in nature; it is the principal constituent of rocks and stones, and exist in a free and almost pure state in flint, agate, chalcedony, rock-crystal, and quartz, the last two being its purest form. Formerly flint (*silex*) calcined and ground, was used as the source of the silica, and hence the name of *flint-glass*. Sand, however, is now employed as the most general and economical source of silica, since it renders the process of grinding unnecessary. At the same time the great variations in the purity of this material render requisite a careful selection for the different kinds of glass, and the manufacturer must choose such as the microscope and analysis show to be most suitable for his purpose. The finest English sands are from Alum Bay in the Isle of Wight, and Lynn on the coast of Norfolk. The French obtain a very superior sand from the forest of Fontainebleau, in the neighbourhood of Paris; and to the purity of this and their other materials the beautiful colour of their glass may be partly ascribed.

The sand, being always more or less impure when brought to the glass-works, is conveyed to an upper room, and thrown into a trough of water, where it is carefully washed. It is then placed in a trough over an oven, and, when partially dried, passes through holes into the oven. When quite dry, it leaves the oven in the state of fine, glittering white particles, like powdered quartz. These precautions are not necessary for green bottle-glass.

Potash and Soda.—The potash for green bottle glass is obtained from common *ashes*, the soda is a refuse soda. Better kinds of glass are made with crude potash and soda-ash, and the best from purified potash and soda-ash. Not many years have elapsed since crown and sheet glass were manufactured from the crude alkali obtained from kelp. The kelp was used simply in combination with sand—the kelp containing soda and potash, and furnishing the necessary amount of lime; but the glass thus produced was of very variable and often most inferior quality. The discovery of Le Blanc in 1792, which effected the conversion of common salt into carbonate of soda, was the commencement of a new era in the history of Continental flint-glass; but the introduction of carbonate of soda, prepared from salt, into the glass manufacture of England, dates only from the year 1831. Ultimately sulphate of soda was substituted, except for plate-glass, the manufacturers of which still adhere to the carbonate. The black bottles of Newcastle are made from common rock-salt and sand from the bed of the river, with the carbonate of lime of the soap-works, and the tank

waste of the alkali makers; but for all better kinds of glass the circuitous combination of silica and alkali is still found necessary. The carbonate of potash is obtained chiefly from Canada, and requires a process of washing previous to use. The state to which it is brought by the process of cleansing is that of fine white grains, differing but little, to an unpractised eye, from the prepared sand.

Lime.—This substance, which forms an important constituent in flint-glass, may be introduced either slaked or burned, or as a carbonate. Limestone, however, that contains ferrous carbonate of iron, must be excluded from the mixture for making white glass. The action of lime is to render the alkaline silicates insoluble, and when rightly balanced by the other ingredients, it promotes the fusion of the whole, and improves the quality, but when added in excess, the glass becomes hard and difficult to work, and subject to devitrification.

Lead is the distinguishing ingredient in crystal or common flint-glass, optical glass, and strass. These glasses are fused from a mixture containing litharge (PbO) or minium—red lead (Pb_3O_4). Red lead is generally preferred on account of its finer state of division, and because it is decomposed in the glass-pot into ordinary protoxide of lead and oxygen, which latter removes many impurities, as, for example, charcoal by oxidation. An excess of lead acts injuriously upon the melting vessels, and besides inducing too great softness in the glass, gives it a yellow tinge.

Baryta.—This substance, in the form known as heavy spar, barium sulphate ($BaSO_4$), is sometimes added to the constituents of common bottle-glass, to render it more easy of fusion.

Alumina, though seldom purposely introduced into glass, is always accidentally present, brought there by the action of the materials upon the clay of the pots in which they are melted. If present in any quantity it is an undesirable ingredient, as, by increasing the number of silicates, it renders the glass more liable to devitrification. Hence bottle-glass, which contains a greater variety of bases than any other kind, is of all the most easily devitrified.

Iron.—Another unwelcome element is iron, which is almost always present in the sand, in the sulphate of soda, and in the chalk.

Arsenic.—A little arsenic promotes the decomposition of the other ingredients, and tends to dissipate carbonaceous impurities not otherwise disposed of; but, in excess, it produces a milkiness in the glass, which time will increase.

"*Cullet.*"—Another substance is added—abundantly produced in every manufactory of glass—namely, a quantity of waste glass, or cullet, which, being more fusible than the raw materials, facilitates the melting. For this purpose the waste glass in the glass-house, and that collected in the neighbourhood, are carefully sorted, cleaned, ground, and incorporated with the mixture *for similar kinds of glass*. Great care must, however, be taken that no broken glass of an inferior kind is mixed with the ingredients for finer glass. The cullet not only incites fusion, but materially aids the union of the bases with the silicic acid.

Oxidizing Materials.—Every description of glass exhibits a tendency to colour, and as any tinge is considered a defect in white glass, certain materials are employed with the special object of counteracting it. To this class of substances belong binoxide of manganese, arsenic, already mentioned, and nitrate of potash. The accidental elements which usually colour the glass are iron and carbon, or carbonaceous matters, and in all cases the substances above-mentioned are employed to neutralize or counteract these by means of oxidation.

For example, if particles of carbon or soot from the fire or flame become mixed and surrounded with the melted glass, these, by their exclusion from the access of air, are prevented burning, and a brown or nearly black colour is produced, which is removed by the conversion of the carbon into carbonic oxide through the influence of the oxidizing or decoloring material. The manner in which manganese acts on the protoxide of iron is similar to its action on carbonaceous matters, which are thus removed in a gaseous form from the melted mass. A few ounces of the binoxide of manganese are, therefore, usually added to the materials for making flint-glass, which is always required in a state of great purity; and from the cleansing action of this material, it has received the familiar title of "glass-makers' soap." It must, however, be used sparingly; for an excess of it produces a compound of silicic acid with sesquioxide of manganese, which communicates a lilac or amethystine tint to the glass, which by exposure to light becomes in course of time very strong. The approved remedy for this, when the error has been committed, is to stir up the coloured mass with a wooden pole, which reduces the sesquioxide to the monoxide, and the lilac colour disappears.

Some manufacturers use manganese, on account of the reddish tinge it imparts to glass, expressly to disguise the bad green or yellow colour produced by the other materials. In this case two tinged glasses are formed, which mask each other's defects, the green and red rays combining together, as supplementary colours, to transmit white light. Indeed, in plate-glass for fine windows, a slight excess of manganese is sometimes allowed, expressly to produce a delicate amethystine tint.

Smalt, a blue glass, is sometimes used, like manganese, to mask the bad colour produced by the other materials. Properly speaking, however, the decoloring agents are those which act by oxidizing the carbon or the protoxide of iron, and thereby actually expelling the lime. Nitrate of potash acts in this way before the glass enters into perfect fusion; arsenious acid, arsenic acid, and their salts, exert their action at a temperature above the fusing point, and are then volatilized.

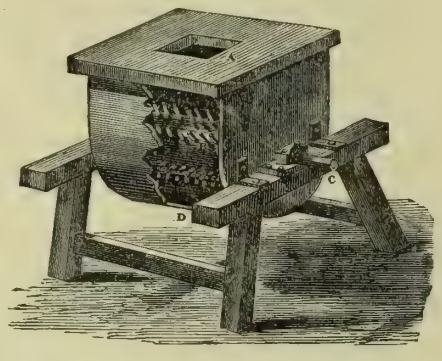
A glass of inferior quality has been made from felspar, and very recently attempts have been made to use part of the slag from iron works in this way, but as yet without much success. Economy of production would require that the ironmasters should

add glass-making to their works, in order to save reheating the slag. This they seem not very willing to do.

The fuel formerly employed in England in the making of glass was exclusively coal, but of late it has been found that, in London especially, many advantages result from using oven-burned coke, which produces less smoke and soot, and is therefore much better adapted for the finer glasses. Some glass-houses have all the requisite accommodation for making coke. In France both coal and coke are employed, and sometimes wood. In Germany wood is generally employed, and in some few places peat. Even the best air-dried wood would fall far short of producing the desired temperature, in consequence of the amount of water which it still retains; and therefore it has been the practice on the Continent, from a very ancient period, to bake the air-dried wood until it begins to become brown, or until the whole of its water has been volatilized. Peat when used in the glass-house must be perfectly dry, and afford only a small amount of ash.

A great saving of time and fuel is effected by

Fig. 3.



carefully grinding and intimately mixing the materials previous to the melting. For this purpose edge-stones and coarse sieves are essential in a glass-house. Until quite recently the mixing and sifting were always performed by hand, and the operation was therefore imperfectly performed, the mixture so produced being little calculated to favour those chemical changes and mutual reactions of the materials which are necessary to the formation of a homogeneous fluid transparent body. To obviate this disadvantage, a mixing apparatus, especially intended for crown-glass, was contrived by CHANCE. This very simple machine, which is shown partly in section in Fig. 3, is made entirely of wood, and consists of a semi-cylindrical chamber, with an opening, A, at the top, for introducing the materials, and another in the semicircular bottom at D, through which they are removed; B is a cylinder in which a number of oblique beaters are fixed, and the whole is made to revolve by a handle or by a shaft from the steam-engine connected with the axis, C.

COOPER'S mixer is a revolving wooden barrel, similar to those employed in the powder factories.

The composition when mixed is termed *batch* or *frit*—the latter word being derived from the circumstance, that during the period when barilla, kelp, and other forms of crude alkali were in use, it was the custom to subject the materials to the preliminary operation of *fritting* or stirring them together under the heat of a reverberatory furnace, thereby effecting partial decomposition, and burning off any carbonaceous impurities; but the introduction of alkali prepared from common salt has, in most cases, removed the necessity of this treatment. One great advantage of fritting consisted in the partial union which it effected between the silicic acid and the metals, so that the latter were not volatilized in the furnace previous to the formation of the glass, and the pots and sides of the furnace were consequently less exposed to the injurious action of their vapours. With the purer materials now employed in the manufacture, the advantages gained by the operation are not generally considered sufficient to compensate for the loss of fuel incurred in producing the high degree of heat required to perform it.

MELTING.—The raw materials, consisting essentially of sand or silica as the base, and alkali as the flux or solvent, having been thoroughly incorporated with a suitable proportion of cullet or broken glass of the same kind, are introduced by means of a clean iron shovel into the melting-pot, which has been previously raised to a white heat. But the whole of the mixture is not introduced at once, for the mass of glass which a pot will hold occupies before fusion, in the state of frit, just twice the space of the melted glass. Not more than one-third of the mixture is therefore introduced at first through the working holes; the temperature is then raised to the maximum, and as the mass subsides by melting, a fresh quantity is introduced, until the pot is filled with melted glass. During the whole period of the melting or "found," the stokers or "teazers" keep the furnace well supplied with fuel, so as to prevent any portion of the grates becoming uncovered, in which case a rush of cold air from below might split some of the pots. At the same time the "founders" are engaged in noting the progress of the fusion, by taking from time to time proofs or drops from the pots, by means of a short rod, flattened at one end, and examining if any undissolved grains of sand are perceptible on refrigeration, and whether the mass, which still contains a quantity of air-bubbles, appears uniform throughout. So long as carbonic acid is evolved in abundance, or during the "boil," the mass is agitated by the escape of the larger bubbles of gas in a manner most favourable to the operation; this motion answers the purpose of stirring, and mixes the compounds of variable degrees of fusibility and density, which are at first produced, with each other. At a later period, when the disengagement of gas ceases, the denser compounds are apt to settle down at the bottom of the pot, where the temperature is about one-fourth lower, and is consequently incapable of preventing the deposition by the production of ascending currents. On the Continent this evil is moderated by stirring with the scooping ladle, or by thrusting a piece of arsenious acid to

the bottom of the pot, and thus causing a forcible expulsion of vapour from that part of the vessel. At the close of the melting process, the contents of the pot are not by any means pure or equally mixed. All the solid matter is dissolved, but the mass of glass is full of small vesicles of gas, and presents a spongy appearance. The surface is also covered by a layer of so-called "glass-gall" or "sandiver," a melted mixture of salts, which have not been volatilized nor combined with silica during the process of melting, and consisting chiefly of chloride of potassium (or sodium) and sulphates, which in consequence of imperfect vitrification have escaped decomposition.

The composition of this saline matter, glass-gall or sandiver, which is skimmed off the surface of the melting materials, and is technically termed "salts," is, according to Richardson and Ronalds, as follows:—

Constituents.	German plate-glass.	Crystal-glass.	Bottle-glass.
Water,	1·65	·10	1·00
Sulphate of sodium,	83·32	90·51	55·92
Sulphate of calcium,	10·35	6·00	25·11
Chloride of sodium,	1 43	·04	·20
Carbonate of sodium,	trace	—	—
Potash,	—	—	trace
Insoluble matter,	3·25	3·35	17·77
	100·00	100·00	100·00

Glass-gall, when occurring in large quantity, is removed with ladles, and is utilized by saltpetre and alum manufacturers, or workers in bronze. In the varieties of glass prepared from purified materials, either no glass-gall is produced, or that which appears is easily removed by volatilization.

Fining.—For some time the glass does not become transparent, the opacity being due to bubbles of air or gas, and to the lime and earthy impurities which do not fuse. The object of the "fining," which is the last process of glass-making, properly so-called, is the removal of these by the subsidence of the heavier particles to the bottom and the escape of gas at the surface. For this purpose the glass must be brought to the most fluid state possible, and the heat is therefore raised and sustained for some hours at the highest point. In Germany this part of the process is termed *heiss-schüren*, or "hot-covering." In forty to forty-eight hours after charging the vitrification is complete. When all the gas-bubbles have passed off, and the sandiver has become transparent and colourless, the temperature of the pot is lowered by diminishing the draught—a process termed *kalt-schüren*, or "cold-covering"—the object of which is to bring the glass from a state of nearly perfect fluidity, in which it could not be worked, to that free viscid or plastic condition necessary for the working. For this purpose the bars of the furnace are plastered up. The great thickness of the walls, and the slow combustion of the fuel, which is supplied in moderate quantity, keep the furnace hot enough to retain the glass in a workable viscid state during the period in which the glass is blown or otherwise shaped into the required forms.

The reactions which take place in the pot or crucible are very easy to understand. For example, if the silica has been mixed with carbonate of sodium and carbonate of calcium, the silica, at a high temperature, seizes on the soda and lime, and the carbonic acid is disengaged. In the same manner, if silica has been mixed with carbonate of potassium and minium, this last returns to the state of massicot, and the silica then combines with it and the potash. There is therefore, in this case, first a disengagement of oxygen, then an elimination of carbonic acid.

These evolutions of gas, which constantly accompany the production of glass, explain the presence of the "air-bubbles" so frequently observed in the vitreous mass. To expel these, the temperature must be raised very high, that the glass may become quite fluid. But as the potash and soda are volatilized at this high degree of heat, much more potash and soda must be introduced into the mixture than the glass is intended to retain.

An elevated temperature is also necessary in all cases where impure alkalies are used. The presence of the chlorides, and even that of the sulphates which melt without mixing with the glass, would occasion in the latter a multitude of white and opaque nodules disseminated through its mass. At a high heat both of these, being lighter than the glass, rise and float on the surface, constituting the principal portions of the glass-gall or sandiver above alluded to. It must be stated, however, that since the salts of soda have been sold at a low price, very little glass-gall has been produced in the manufacture of the ordinary kinds of white glass; in bottle-works this impurity always occurs, because crude sodas are employed.

Faults in the Glass.—Notwithstanding all the precautions that may be taken, air-bubbles frequently remain, and generally exist in great number when the fining process has been obstructed by too great difficulty of fusion in the glass. They are technically tern ed "seed," "blibe," or "blister."

Two further accidents to which the glass is liable are known as "threads" or "strings," which are generally contracted during the blowing, when cold particles of glass drop into the viscid or imperfectly melted metal, and not having time to undergo fusion remain hard, and appear as unsightly projections from the blown vessels.

"Waves" and "striæ" are faults of too common occurrence, arising from a want of homogeneity in the vitreous mass. The latter of these terms are applied to the effect produced when the density of the glass, in consequence of imperfect fusion, is not uniform throughout, and all the parts, though equal in transparency, do not refract the light equally; and consequently images of objects seen through the glass appear out of place or distorted. Waves are superficial and protuberant striæ, which always occur when the glass is blown too cold.

A not less serious evil arises from the action of the alkaline vapours upon the constituents of the sides or roof of the furnace, particularly when chloride of sodium or sulphate of soda is used in the manufacture. The volatilization of the alkali, whether soda or potash, produces a rapid vitrification of the

bricks of the vault, and hence drops of coloured glass, known by the name of "tears," occasionally fall into the pots.

GLASS-HOUSE AND FURNACES.—The glass-house in which the processes of melting and blowing are performed, is usually built in the form of a truncated cone, open at the top, of 60 or 80 feet in height, and 40 or 50 feet in diameter at the base. In the centre of the area is situated the melting furnace, capable of holding from five to ten glass-pots or crucibles for fusing the materials. The grate of the furnace is nearly on a level with the floor of the glass-house; and the ashpit or "cave" is a subterranean passage, extending from each side of the furnace to the exterior of the building, so as to catch the wind from as many aspects as possible. The particular arrangements of the glass-house, and the construction of the furnaces, are sometimes varied according to the kind of glass prepared.

Fig. 4.

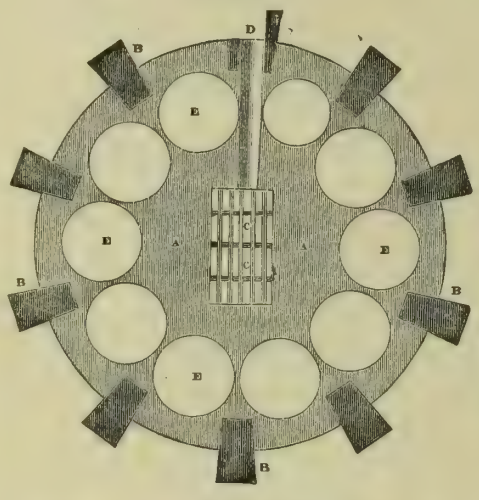


Fig. 5.

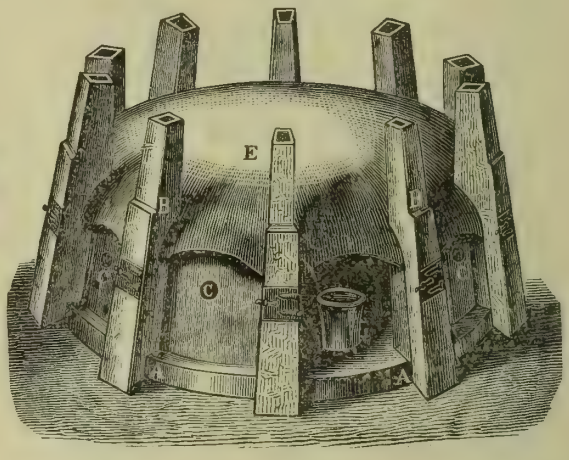
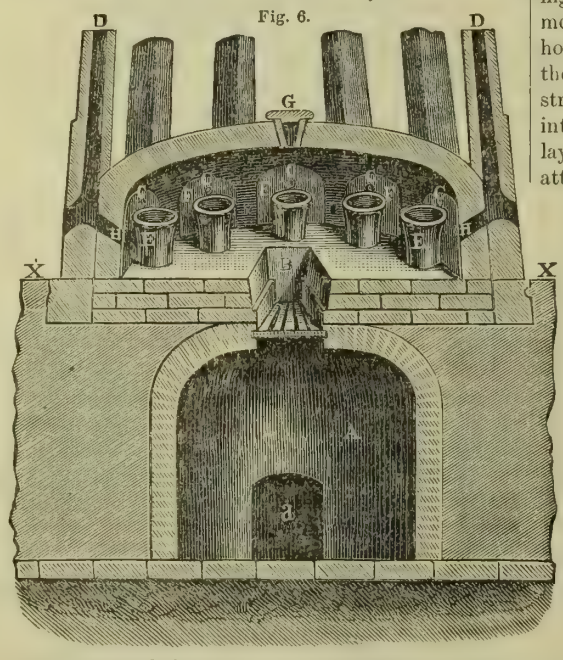


Fig. 6.



The arrangement of a flint glass-house furnace is shown in Figs. 4, 5, and 6, where the furnace is represented as containing ten pots, E E. There are as many flues, B B, as pots, one flue being placed between every two pots; and immediately abreast of each pot, and between two flues, is an aperture called the working hole, which is used for introducing the raw materials, and taking out the glass or metal. The coals are shovelled through a square hole, D, Fig. 4, upon the grate, C C, in the centre of the furnace. The grate bars are supported by two strong iron sleepers, and are protected from the intense heat by being previously covered with a layer of clinkers or potsherds; but as the furnace attains its maximum heat, sufficient clinkers are formed to serve the purpose. All round the grate-room a bank, A, Fig. 5, is raised, termed the "siege," on which the pots are placed, so that the fire lies, as it were, below the bottom of the pots, and in the centre of the furnace. The sides of the furnace are a little higher than the top of the pots, and the arch or crown is made as low as is consistent with durability.

Fig. 5 is an exterior view of the brick dome, and Fig. 6 an interior sectional elevation of the same, showing the position of the flues, arches, and cave. In Fig. 5 the letters A A indicate the sole of the furnace; B B, the flues; C C, openings or arches, which, after introducing the pots, are built up, leaving only working holes; E is the roof or dome. In Fig. 6, *a* is the air-tunnel below the furnace, it opens into the great ashpit, A; B, pit of furnace, with grates below; H H, flue or linnet holes, through which the flame, not being allowed to issue from the centre, passes up the flues, and from thence into the funnel and chimney shaft; C C are the working holes; E E the pots; and F F the charging openings; X X is the ground level.

The dimensions of a convenient flint-glass melting

furnace are as follows:—A furnace for ten pots of 36 inches diameter is 12 feet 7 inches in interior diameter, including the flues; the height to the inside of the dome is 4½ feet; each of the arches is 3 feet 1 inch by 3 feet 3½ inches to the highest part. The fire is regulated by the stoker or "teazer"—from the French *tiseur*—who can raise the heat of the furnace to the highest pitch by opening holes at the bottom of the grate. A ten-pot furnace consumes from 18 to 24 tons of coal per week.

The construction of the m lting-furnaces in a glass-house is attended with many difficulties, against which it is almost impossible to provide; and the wear and tear becomes a serious item to the manufacturer. The prevailing temperature of a glass furnace, about 20,000° Fahr., presents in itself a serious difficulty; but in cases where open pots are employed, this is materially increased by the volatility of the alkalies, which amounts to nearly 25 per cent. of the potash. In ordinary cases, three years is the usual duration of these furnaces, except in flint glass-houses, where they last longer, from the lower melting point of the materials, and the peculiar shape of the pots.

The sides of the furnace are constructed of bricks, formed in moulds made for the purpose. The best fire-clay, mixed with the remains of old pots coarsely ground, is the material employed for making these bricks; but these clays would be much improved for this and many other purposes, by the addition of some coarse sand or ground pure sandstones. The roof is generally made of sandstone alone, of a coarse grit, and very porous. No cement is employed in the arch, the expansion of the stone, and the partial fusion of the interior surfaces afterwards, bind the whole sufficiently well together.

Crown and plate-glass furnaces are similar to the flint; they are likewise placed in the middle of the cone, but contain only from four to six pots, each of the capacity of half a ton of metal.

Besides the main or melting furnace, a glass-house contains a variety of furnaces and arches adjoining or around the inside of the cone, for different subsidiary operations. The "calcar arch," for burning frit, now little used, is a common reverberatory furnace, about 10 feet long, 7 feet wide, and 2 in height. In crown-glass works there are also the "blowing furnace," the "bottoming hole," and the "flashing furnace," besides an aperture in the latter termed the "nose-hole."

Another form of furnace which is in use on the Continent is shown in Fig. 7. CC is the melting oven; it is strengthened by being surrounded with pillars, AA, which also in some degree protect the workmen from the heat. BB are the working holes; DD, doors to the side ovens; EE, arches beneath the side ovens, leading to the fire grate. Fig. 8 is a horizontal section at the fire level; *uu* are steps leading to the arches beneath the furnace; *nn*, stoke holes; C, the fire grate; O, the furnace chamber; III, the shelf on which the pots are placed; *iii*, the working approaches; *lll*, the pillars. Fig. 9 is a vertical section along the line A—B, Fig. 8. GG are the steps leading to the arches FF. EE are the stoke holes; C, the fire; D, the ash-pit; the pots, II,

Fig. 7.

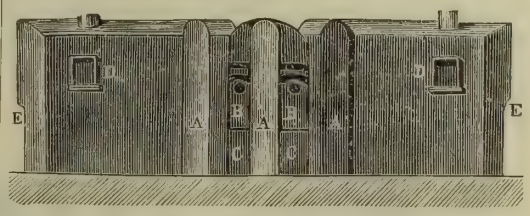


Fig. 8.

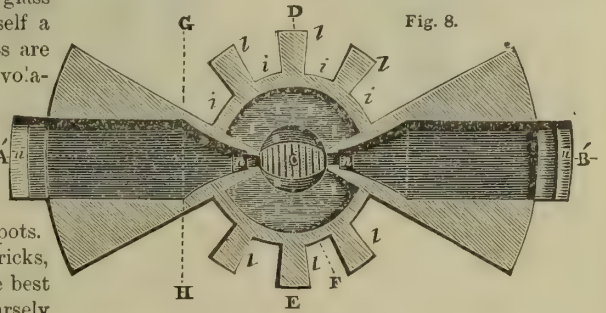


Fig. 9.

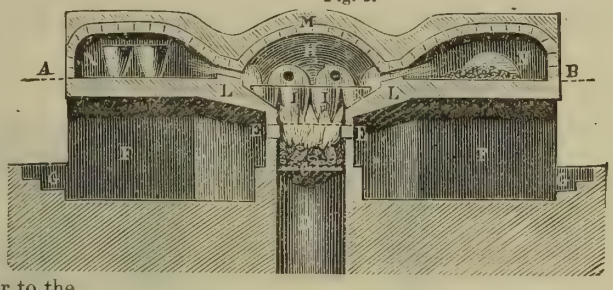
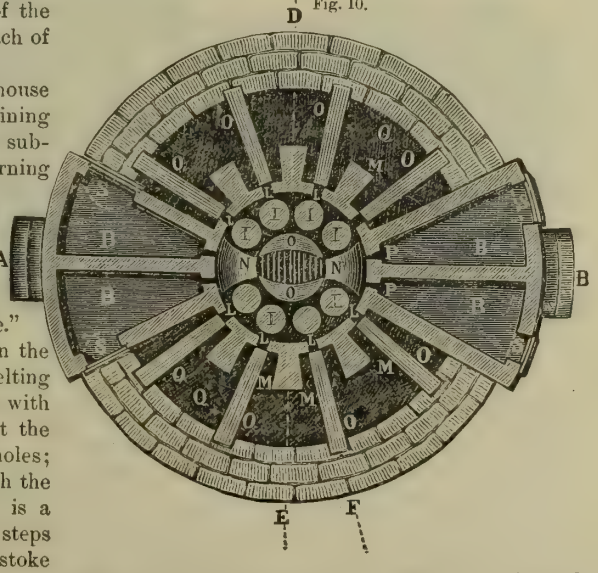


Fig. 10.



stand on the dotted line seen in Fig. 8. H, the arch of the melting oven; LL, flues leading the flame

and heated air to the calcining and annealing ovens, NN. M shows the contour of the brickwork. Fig. 10 is a horizontal section of the furnace along the line A—B, Fig. 9. LL are the working holes, one of which corresponds with the seat of each glass pot, II; OO is the furnace mouth; NN, small arches covering the stoke holes; PP, flues leading the flames into the ovens BB; SS, doors through which the materials

Fig. 11.

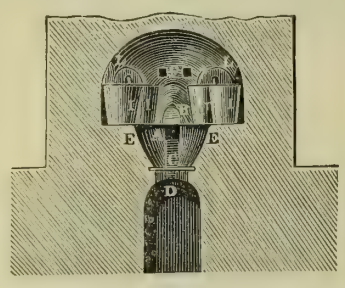
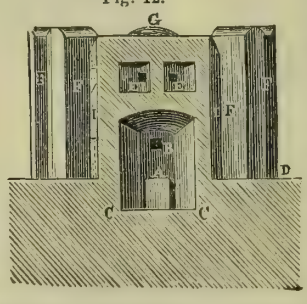


Fig. 12.



are introduced; M, the pillars (seen at A, Fig. 7, and *l*, Fig. 8); OO, the staging over the pits, Q, upon which the workmen stand.

Fig. 11 is a vertical section along the lines D—E in Figs. 8 and 10; A is the stoke hole; B, drawing hole; C, the fire; D, the ash-pit; E, pot shelf, with pots, II, F, flues to the side ovens; LL, working holes.

Fig. 12 is a vertical section along the line G—H (Fig. 8). A is a block of masonry upon which to rest the pots when filling the furnace; B is the stoke hole; EE is a section of flues to the side ovens; FF, pillars; G, roof of the melting oven; D, ground level.

Glass making was amongst the earliest industries to adopt SIEMENS' regenerative furnace.

A very simple arrangement of the apparatus is shown in Figs. 13 and 14. The coal (which may be any inferior kind) is converted by burning, with limited access of air, into carbonic oxide in the generator, Fig. 13. This is conveyed through the "regenerator," Fig. 14, to the furnace where it is burnt—the heated products of combustion passing out through a second regenerator, when the first regenerator has cooled down, the second will have become intensely heated; the current of gas is then reversed, No. 1 becomes No. 2, and No. 2 becomes No. 1. The arrows show the course of the gas.

GLASS, Plate I., shows the modification which is now most frequently adopted.

In the application of the regenerative gas furnace to glass melting the pots hitherto employed are done away with, by making the furnace a tank divided into compartments, the flame either taking a horse-shoe form, leaving the furnace by an exit port close to the port of admission of the gas and air, or else

Fig. 13.

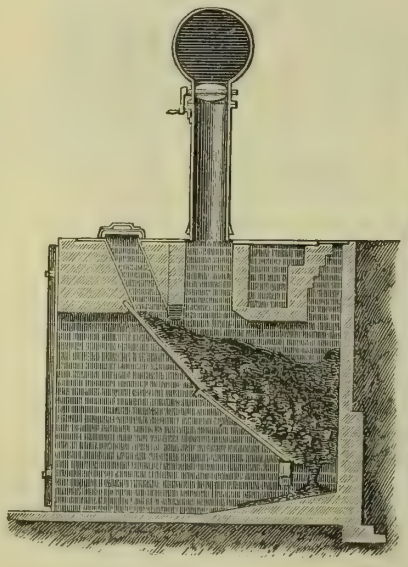
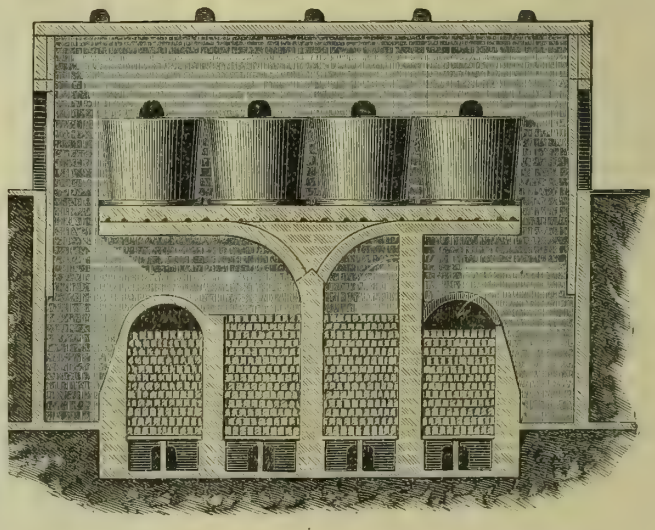


Fig. 14.



playing across the furnace. The temperatures of the various portions of the furnace is regulated according to the various stages of preparation of the glass in the several compartments, the ports being increased either in dimensions or number where great heat is required.

In the melting and working out of glass, it is of importance that the operation should be carried on in a continuous manner, crude materials being supplied at the one end of the melting tank, and the refined glass being worked out at the other end. The glass as it becomes melted sinks towards the bottom of the tank where it is purest, the less pure and imperfectly melted and incorporated portions floating above. It is therefore advantageous to prevent the passage of the lighter matters towards the working out end of the tank, and in working out the glass to draw it from a lower level.

In order to produce this effect either bars or girders of fire-clay, or other refractory material, are

Fig. 1.

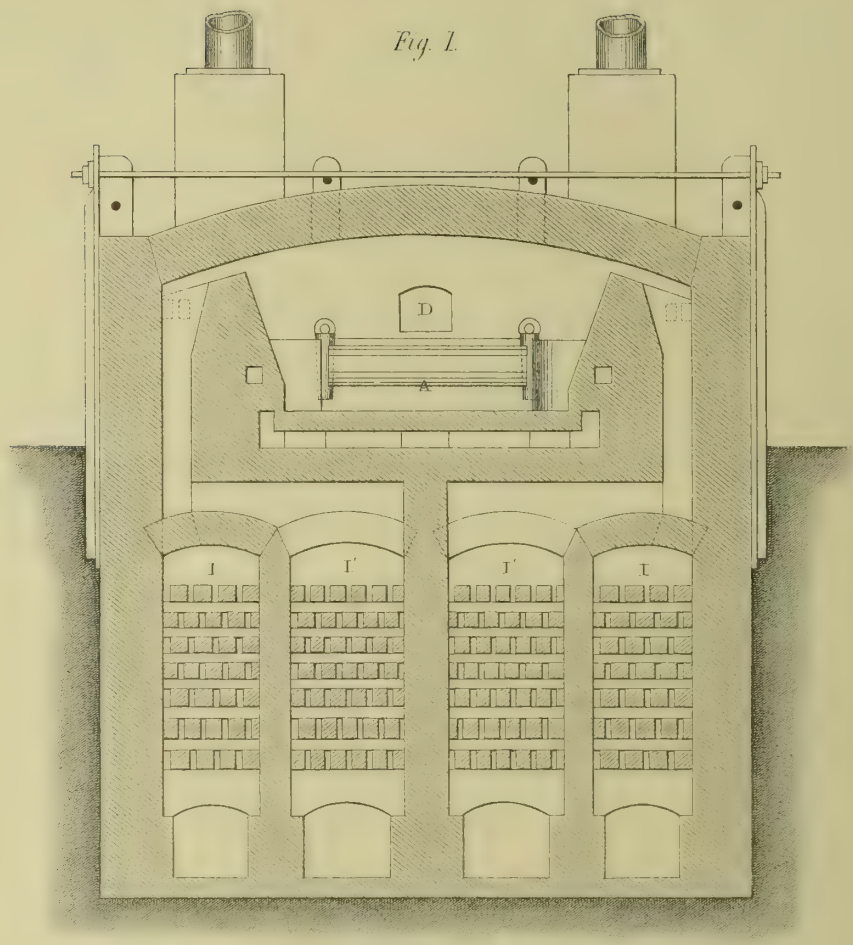
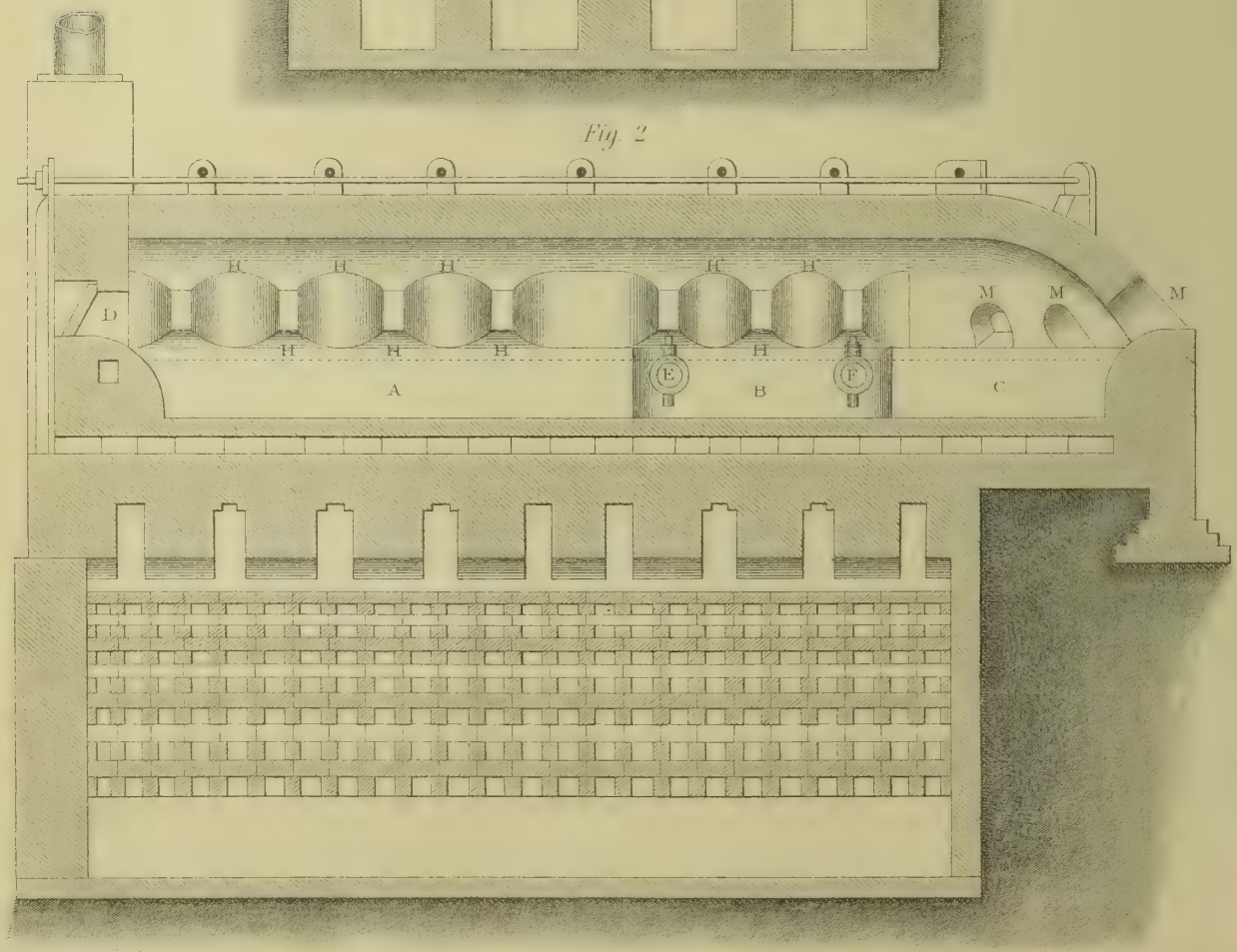


Fig. 2



floated on the surface of the molten matter in the tank, and placed there transversely at intervals so that they form floating bridges, dividing the upper stratum of the molten matter into two or more compartments; or else fixed bridges are employed with hollow spaces running through them from end to end for the passage of a current or currents of air. Thus the imperfectly melted or impure material is kept at the supply end of the tank, and only the more thoroughly melted and pure matter is permitted to flow towards the working out end, by passing downwards and under the bridges. Advantage is thus taken of the variable density of the glass in the different stages of its preparation, to keep the molten material separate in the several compartments, the flow being kept up by the pressure of new material in the charging compartment.

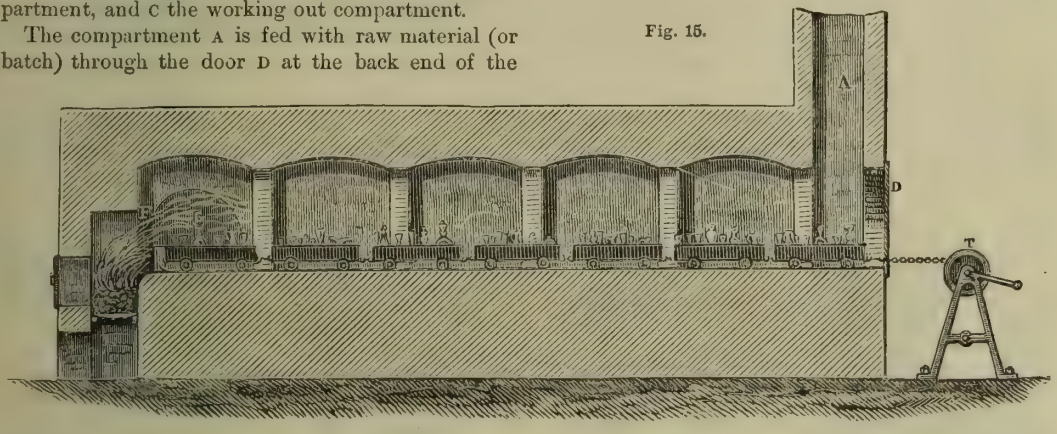
The following is a brief description of this furnace, reference being made to the accompanying Plate, in which Fig. 1 is a transverse and Fig. 2 a longitudinal section of the furnace.

A is the melting compartment, B the refining compartment, and C the working out compartment.

The compartment A is fed with raw material (or batch) through the door D at the back end of the furnace; it is separated from the compartment B by the floating bridge E, under which the partially melted glass passes to reach the latter. In this latter compartment the metal, by the influence of the higher temperature maintained on its surface, is completely purified and sinks to flow under the bridge F in a complete workable condition. Suitable provision is made, by means of air passages, to keep the sides of the tank of the requisite temperature, to prevent any egress of glass through them, and the floating bridges E and F are renewed as often as necessary.

The regenerative gas furnace is employed, and the gas and air ports, H H′, leading from the regenerators, I I′, respectively are arranged along each side of the tank, so as to cause the flames to play across the furnace. The temperature of the different parts is regulated according to the various stages of preparation of the glass in the several compartments, this regulation being effected by constructing the gas and air ports of larger dimensions, or increasing their number where the greatest heat is required; it is

Fig. 15.



also facilitated by means of division walls (not shown in the plate), which may be built over the floating bridges to separate the compartments. The temperature of the working out compartment, C, is controlled by regulating the draught of the furnace chimney, by diminishing which more or less flame must necessarily pass from B, over the floating bridge F, into C, and through the working holes M.

The principal advantages resulting from the use of the continuous melting furnace are—an increased power of production, as the full melting heat may be employed without interruption; an economy in working; a greater durability of the tank or furnace; and a much greater regularity of working.

The reason of the greater durability of the tank is not only due to the uniform temperature maintained, but also to the circumstance that the batch is filled in in such quantities as not to come into contact with either the sides or the bottom of the tank, which consequently are not suddenly cooled or eaten away by the mixture; also to the fact that each compartment of the tank is subjected only to the requisite amount of heat necessary for the purposes carried on therein.

The annealing oven comes next in importance to the melting furnace. This name is given to a low arch, open at both ends, in which the manufactured goods are allowed to cool gradually. The arch is usually about 60 feet in length, 5 feet wide, and not more than from 1 to 2 in height. Adjoining the door or receiving end is a small furnace on each side, by which the temperature at that end is maintained just short of a melting heat; but as there is no other heating power, the arch or oven experiences less and less of the heat as the distance from the mouth is greater, until, at the remote or discharging extremity, the temperature is scarcely higher than that of the atmosphere. There are usually from two to four of these annealing arches placed side by side. Along the floor of each is a miniature railway, upon which two rows of iron trays, called "leer pans" (G, Fig. 15), travel from the hot to the cooler end, D, where they are taken out. The pans are moved slowly along the leer by means of a chain, T, or sometimes they are gradually pushed forward by the trays last put in. F is the opening for filling the trays, A the chimney shaft. The fuel employed is coke, which imparts the most regular

heat for annealing, and is the freest from smoke, the carbon of which, when coal is used, injures the colour of the glass. The time required for proper annealing varies from six to sixty hours, the weighty articles requiring the most heat and time. The hotter the goods enter the arch the better, and on this account large articles, before being introduced, receive a final re-heating at the mouth of an empty pot, heated by beechwood, and called the "glory-hole." Much of the success of annealing depends on the proper direction of the draught, which ought to pass over the fuel of the leer toward the leer chimney at the cooler end, so that the hot air may always radiate in the downward current upon the goods. When an upward or contrary current of wind drives back the heated air from the cool or chimney end toward the fuel at the upper end, where it comes into contact with the hot articles just introduced, great losses from breakage often occur.

Kilns, which differ from leers in being closed at the further end, were formerly in general use for annealing goods intended for deep cutting, the kilns, when filled, being carefully closed up along with the burning fuel. The time required for cooling in this case was usually about a week. To avoid so much delay, the kilns have been superseded by the use of iron covers or a bedding of sand in leers; also by lengthening the leer fire-places, and not filling the pans with glass too quickly.

Fig 17.

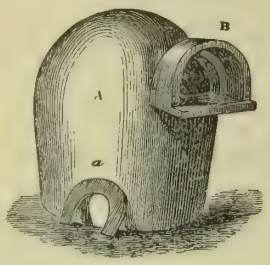
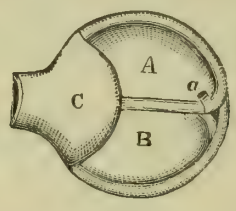


Fig. 18.

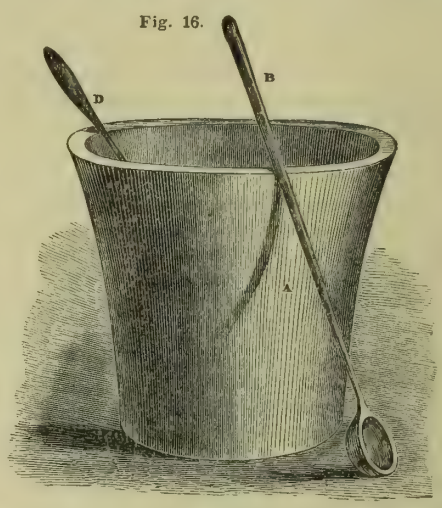


glass, and the stirring rod, D. The pots for flint-glass are hooded or covered at the top, and have a mouth, B, in front like a muffle, as shown in Fig. 17; but those for crown, plate, and bottle-glass are open. The horse-shoe shaped piece of fire-clay, *a*, is inserted in the mouth during the melting, to diminish the aperture.

Siemens' pot is shown in Figs. 18, 19, and 20. The raw material is put into A; as it melts the glass flows through the opening *a* into the compartment B; here it is fined, and parting with its gas bubbles, scum, &c., the pure glass passes by the outlet *b* into the chamber C, when it is fit for use; *c* is the working opening.

The Pots.—The crucibles, or pots, in which the vitreous mixture is melted require great care to be taken in their preparation. Those used for bottle, crown, and plate-glass have the form of a truncated

Fig. 16.



cone, A—Fig. 16—the narrow end being the base. Their depth is usually 4 feet 6 inches; their diameter at top, from 4 feet to 4 feet 6 inches, and at the bottom, about 3 feet 4 or 6 inches. In the same figure are shown the ladle, B, for taking out the

Fig. 19.

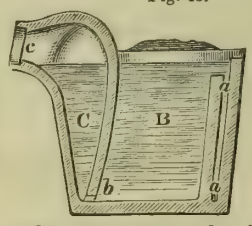
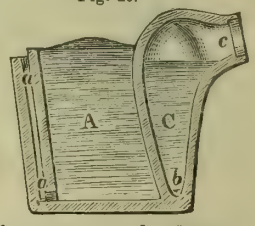


Fig. 20.



Glass-pots are made of clay as pure and refractory as can be obtained, free from every trace of lime and sulphide of iron; and the less oxide of iron the better. The kind of slate clay dug out near Stourbridge is decidedly preferred to all other compounds found in this country. The clay is mixed with varying proportions of the remains of old pots, and the *tempering*, or previous preparation of the mixture, requires great attention. A certain quantity of the ground materials, after being mixed with water, is stored away in large wooden bins or receptacles, and turned over from time to time, during which a workman treads it under his naked feet. This *kneading* of the clay renders it very uniform and free from particles of air. The following is the composition of some of the clays employed:—

	Stourbridge. Richardson.			Stourbridge. Muspratt.	Rhuabon. Muspratt.
Silicic acid	68·05	63·70	64·10	63·99	61·77
Alumina	18 85	20·70	23·15	20·84	18·97
Lime	·80	1·30	—	·30	1·53
Magnesia	—	—	·90	·94	·91
Iron	5·10	1·00	1·85	·75	·17
Water	6·00	10·30	10·00	11·67	14·79
Loss	1·20	3·00	—	1·51	1·86

The proportions given by Barruel as most suitable for glass-pots of any description, are 13 parts of crude aluminous clay, 12 parts of calcined silicious clay, and 3 parts of the remains of old pots. The last-mentioned material assists the more regular drying of the pots, and renders the whole body more porous and less liable to crack by heat.

When the mass has been kneaded three times over until it acquires a pasty consistence, it is rolled into small pieces about the size of a sausage, and these wet rolls are placed together upon a wooden or leaden slab, to the thickness of 4 inches, to form the bottom. It is then turned up at the edges, and built, layer above layer, in successive rings, all formed by the eye of the workman without the use of a mould. When the pot has been finished, the sides are made smooth by means of small wooden scrapers.

After the glass pot is formed, it is allowed to remain for a considerable time in an apartment heated by a flue to about 80°, in order that it may be slowly dried in an equal manner throughout its whole thickness. Two or three years is the time allowed by some manufacturers for this gradual desiccation.

Before the pot is *set* in the furnace, it must be subjected to an annealing process, which consists in gradually increasing its temperature during several days to bright redness. This is usually done in a reverberatory constructed for the purpose, the fire in which must be raised very slowly, not more than a shovelful of coals being introduced at a time, and that at regular intervals. While at a bright red or even a white heat, the pot is quickly transferred, with the assistance of adequate machinery, into its seat in the hot furnace; a part of the face of which must be pulled down, to allow of the ready extraction of the old pot and introduction of the new one. Before the pot is used it is *glazed*, as it is technically termed, before being filled with materials; that is, some cullet or old glass is thrown into it and spread over the sides in a molten state. This penetrates to the depth of a few lines into the substance of the pot, and forms a hard, difficultly fusible enamel, which protects the pot from the further action of the substances added.

A small lump of coal, thrown against its side, tests the soundness of the pot. If when struck it rings well, its future is promising; but if it returns a dull sound, it will probably be short-lived in the furnace.

The average duration of the pots, when thus fixed, is about seven weeks. Some attain the age of ten or twelve; while others, as every manufacturer well knows, terminate their existence prematurely, either from the naturally defective constitution of the pot or from bad treatment in the pot-arch, or more frequently from its having been *starved*—that is, exposed to a current of cold air in the furnace through the neglect of the attendant. The breakage of a pot often disturbs the furnace to such an extent that the breakage of others frequently follows, and many weeks will sometimes elapse before the disorganization thus produced can be rectified. The loss of the pot and the contained "metal" is nothing as compared with the injury which the glass in the surviving pots, and these pots themselves, are apt to sustain.

Green Bottle-Glass.—The materials for common glass bottles are coarser than for any other kinds of glass; and in consequence the elements which enter its composition are more numerous, consisting, as already stated, of silica, lime, potash or soda, oxides of iron and manganese. These last oxides communicate a colour to this glass, which owes, at the same time, a part of its characteristic hue to the charcoal. No decoloring materials are used, and it is melted in open pots, even when coal is used as the fuel.

In choosing ingredients for bottle glass, economy is the chief object, colour and appearance being of no moment. Little soda or potash is admitted into the composition of this description of glass.

The primary materials of the manufacture of this kind of glass are yellow and ferruginous sand, residues proceeding from the lies of the soap and soda works, lixiviated ashes, common ashes, and clay.

The coloured sands are even preferable to white sands for bottle glass, the oxide of iron, which colours them, performing the part of a flux. They do not require any washing or other preparation; but any coarse foreign substances, such as pyrites, flints, &c., are separated from them. For this purpose they are dried, and passed through a sieve. The clay best adapted for bottle-glass is a yellow marly earth; it is furnace clay, containing therefore alumina, silica, carbonate of lime, oxides of iron and manganese; it has not much of a binding quality, and is easily reduced to powder when dry, which facilitates the mixtures.

The ashes are generally obtained from domestic fires. They are sifted and dried before using.

The following is the usual proportion of these materials:—For

ENGLISH BOTTLE-GLASS.

100	lbs.	lixiviated ashes.
40– 90	"	kelp.
30– 40	"	wood-ashes.
80–100	"	clay.
100	"	cullet.

ORDINARY FRENCH BOTTLE-GLASS.

30– 40	lbs.	varec.
160–170	"	lixiviated ashes.
30– 40	"	fresh ashes.
80–100	"	clay containing iron.
100	"	broken glass.

The amount of cullet is not particular; it is increased for the first and second melting, when new pots are used. If a very argillaceous sand is employed it is necessary to suppress the clay, and supply lime by a suitable addition of chalk. Crude soda may be used to replace the potash yielded by the varec, but in this case care is taken to add to the mixture a certain quantity of fresh ashes, that the glass may not be wanting in potash.

The proportions given in the preceding recipes, as

well as those that follow, are calculated for 100 lbs. of sand:—

FOR CHAMPAGNE BOTTLES, ACCORDING TO JAHKEL.

200	lbs.	felspar.
20	"	lime.
15	"	common salt.
125	"	iron slag.

ORDINARY GREEN BOTTLE-GLASS.

72	lbs.	lime.
280–278	"	lixiviated wood-ashes.

DARK GREEN BOTTLE-GLASS.

20	lbs.	dry Glauber's salt.
18	"	soap-boilers' flux.
1	"	Scheffel—Pruss.—lixiviated ash.
39	"	glass from the hearth.
179	"	green cullet or broken glass.
45	"	basalt.

White Bottle or Chemical Glass.—Under this head may be included white glass for medicinal bottles and chemical purposes, refractory Bohemian glass for tubing, &c., and foreign crown. The most beautiful material for bottles is furnished by flint-glass or crystal, but these are only intended for ornamental articles or vessels for the table, and will be alluded to under Flint-glass.

The general character of white bottle-glass consists in this, that it is composed of purer materials than the green; decoloring matters are used, and the materials are selected as free from iron and alumina as possible. Moreover, in this case the glass is subjected to a thorough fining process. The following are general standards of composition for different varieties of glass of this description:—

FOR APOTHECARIES' PHIALS.

100	lbs.	white sand.
30– 26	"	potash—impure.
17	"	lime.
110–120	"	ashes.
·25–·5	"	binoxide of manganese—cullet.

BOHEMIAN CRYSTAL FOR GRINDING.

100	lbs.	white sand.
0– 60	"	purified potash.
8	"	chalk.
40	"	broken glass.
·75	"	manganese.

SEMI-WHITE.

100	lbs.	sand.
100	"	crude soda, containing lime.
100	"	cullet.
·5– 1	"	manganese.
100	lbs.	sand.
30	"	potash.
18	"	lime.
		decoloring matters.

CLEAR WHITE.

100	lbs.	sand.
65	"	calcined potash.
6	"	fallen lime.
100	"	white cullet.
·5	"	manganese.

WHITE GLASS FOR CHEMICAL PURPOSES.

100	lbs.	white sand.
41·4	"	potash.
17·5	"	lime.

Bohemian Glass.—The coarser qualities of this kind of glass are analogous in composition to bottle-glass, and are distinguished by comparative freedom from colour, great lightness, and their very refractory nature, which renders them capable of resisting not only high heats, but sudden changes of temperature. Hence the value of this glass for chemical purposes, such as tubing, retorts, &c. Its lightness, and the almost total absence of colour, cause it to be highly valued on the Continent for table-ware, where it is also employed to make costly windows, for covering engravings, &c. In common with crown-glass, it is also peculiarly fit for optical instruments, in which it is employed to achromatize the flint-glass. These remarks apply to the finer qualities, for which Dumas gives the following choice of proportions:—

Quartz in powder, or fine silicious sand, washed with hydrochloric acid,	100	110	120	100
Purified carbonate of potash,	60	64	66	75
Very pure carbonate of lime,	20	24	25	50

In a Bohemian glass of old manufacture, Dumas found

Silica,	69·4	= 36 oxygen.	
Alumina,	9·6	= 4·48	9·04
Lime,	9·2	= 2·57	oxygen of
Potash,	11·8	= 1·99	the bases,

which would give exactly the proportion of 1 : 4 between the oxygen of the bases and that of the acid. On the whole, Bohemian glass may be described as a silicate of potash and lime, with a small proportion of alumina, magnesia, and other ingredients. This will be obvious from the following analysis of a glass, taken by M. Perdonnet from a manufactory at Neuvelt, and analyzed by M. Gros in the laboratory of the School of Mines at Paris:—

Silica,	71·6	= 37·1	Oxygen.
Lime,	10·0	= 2·81	
Potash,	11·0	= 1·86	
Alumina,	2·2	= 1·02	= 7·83
Magnesia,	2·3	= 0·89	
Oxide of iron,	3·9	= 1·20	
Oxide of manganese,	0·2	= 0·05	
	101·2		

Here it will be noted, that the silica contains about five times the aggregate oxygen of the bases. It will be observed also, that in Bohemian glass potash takes the place of soda.

Foreign Crown-Glass.—The name of crown-glass is limited in this country to that which is formed into circular plates by the process of blowing, but the crown-glass of the Bohemian glass-houses is generally moulded into different shapes, with a view to grinding and polishing. Regarded in this light, the foreign crown, properly so called, is rather distinguished by its composition than by the methods of manipulation adopted in its manufacture. Like the coarser Bohemian glass, it is a silicate of potash and lime; whereas, in the English crown, soda is employed, either in the shape of sulphate or carbonate. Dumas analyzed a good crown-glass of German manufacture with the following result:—

	Centesimally.		Oxygen.	
Silica,	62·8	=	32·6	
Alumina, oxide of iron and of manganese,	2·6	=	1·3	
Lime,	12·5	=	3·5	8·4
Potash,	22·1	=	3 7	

So that in this case the silica contained about four times more oxygen than the bases, and the quantity of oxygen in the lime and potash, the two principal bases, was nearly the same.

As the beauty and value of this glass depend upon its absolute limpidness, the most careful selection of materials, both for the mixture and the pots, and a protracted and assiduous process of fining are required. It is not easy to arrive at a certainty of success in its manufacture. To obtain it without colour, potash must be used, and not soda, and no oxide of lead; but lime must be added, since by forming a glass with merely a potash base, the glass would be soluble in boiling water, and consequently hygrometrical. This would be a serious disadvantage; for spectacle-glasses or other lenses so formed would constantly tarnish by the deposit of a film of aqueous vapour, and in the space of a few years would altogether lose their polish. This inconvenience is avoided by adding to glass with a base of potash a certain quantity of lime; but then arises a not less serious evil, a proneness to devitrification. Glass with a base of potash and lime, submitted to the prolonged annealing which thick masses intended for large lenses require, is apt to assume the milky aspect which indicates a commencement of crystallization in the mass. Thus the manufacture of crown-glass, as well as that of flint-glass—the two glasses indispensable for the preparation of achromatic objectives—both present the most serious difficulties, although from very different causes.

Window-Glass.—The glass which has long been in common use for window-panes is that which is generally known as *English crown-glass*, in the manufacture of which a large globe is first blown at the end of the pipe, and this is converted by a rapid rotatory motion into a circular plate or disc thickened at the centre. Until a comparatively recent period this was the only method employed in the manufacture of window-glass in this country; but latterly the Continental method has been extensively introduced, which consists in forming the globe into a cylinder, and then, after cutting it up in a direction parallel to the axis, flattening it out into a broad sheet, from which it has received the designation of *British sheet-glass*. *Plate-glass*, or that which is cast into sheets by pouring the liquid metal on a flat surface, is now much used for the same purpose. *English Crown and Sheet-glass* are composed of precisely the same materials, and differ only in the mechanical operations by which they are brought into form. Chemically speaking they are the same, except that the nature of the crown-glass manipulation requires a smaller quantity of lime.

The materials employed for the manufacture of English crown and sheet-glass—in other words, of window-glass — are chiefly silica, soda, and lime. This glass differs, therefore, from the foreign crown and Bohemian glass in the circumstance, that soda, as the cheaper alkali, is generally substituted for potash. Sometimes, however, though rarely, a mixture of the two is employed. Alumina, oxide of iron, and oxide of manganese are also found in window-glass, but only as accidental ingredients. It is true, indeed, that when iron is present, as is almost always the case, the binoxide of manganese is purposely introduced to neutralize its effects; and a little arsenic is generally added to promote the decomposition of the other ingredients.

To lay down any standard proportions for window-glass is almost impossible, as no two manufacturers use the same; and even in the same works the melting powers of the furnaces may so far differ as to render necessary, for the production of the same glass, variations in the proportions of its elements. The following are mixtures used in some English manufactories:—

	Lbs.	Lbs.	Cwts.
Sand,	560	448	16
Chalk,	154	146	5
Carbonate of soda,	119	168	5
Sulphate of soda,	63	17	1·25
Arsenic,	2	2	0
Cullet,	448	448	16

The introduction of carbonate of soda, prepared from salt, into the glass manufacture of England, dates from the year 1831. Previously to this kelp was employed as the source of alkali.

The following is a French composition, which gives a window-glass of fine quality:—

	Parts.
Sand,	100
Chalk,	35 to 40
Dry carbonate of soda,	28 to 35
Broken glass,	60 to 180
Binoxide of manganese,	0·25) Sometimes in
Arsenic,	0·20) larger quantity.

The oxygen of the bases in this glass is generally to the oxygen of the acid as 1 to 4.

Bastenaire gives the three following compositions, which Dumas considers too rich in alkali, and too poor in lime:—

	Parts.
I.—White sand,	100
Good potash,	65
Lime slaked in the air,	6
Fragments of white glass,	50
Arsenious acid,	1
Oxide of manganese,	0·30
II.—Very white sand,	100
Good soda,	90
Red oxide of lead or minium,	5
Broken white glass,	100
Carbonate of lime,	5
Oxide of manganese,	0·40
III.—White sand,	100
Good soda,	80
Carbonate of lime,	8
Broken glass,	110
Oxide of manganese,	0·20
Oxide of cobalt,	0·10

A beautiful window-glass is produced by the following composition by Dumas:—

	Parts.	Parts.
Sand,	100	100
Dry sulphate of soda,	44	58 to 75
Charcoal in powder,	4	4·5 to 5·5
Slaked lime,	6	13 to 15
Broken glass,	from 20 to 100	25 to 100

Plate-Glass.—Dodd justly remarks that a better name than *plate*-glass would be *cast*-glass, since the former is vague in its acceptation, and might be

applied to any kind of glass in sheets. This beautiful form of glass is formed by being *cast* or *founded* upon a smooth table while in a liquid state, and is totally independent of the process of blowing. It is not generally known, however, that originally all plate-glass was made by blowing; and that in this country it was not till 1773 that the British Plate Glass Company first began to make plate-glass by casting, although this process had been in use in France for nearly a century. The method of blowing plate-glass was very similar in principle to that of sheet-glass, differing only in some mechanical contrivances to assist the workmen in handling so much heavier a piece. The plates formed by this method, however, were much smaller than can be executed by the casting process, which commonly exceed 10 feet in length, and are about half an inch thick.

The principal consumption of plate-glass is for mirrors, the manufacture of which dates from the earliest introduction of glass-works into Europe. Mirror-glasses were for many years the object of an important commerce to Venice, the only city which could produce them. The manufactory, which was situated on the island of Murano, produced, however, only sheets prepared by blowing, and this was the process imported into France in 1665, along with the art of covering plates of glass with tinfoil, which had long been exclusively possessed by the Venetians. The largest mirror-glasses which could be made in this manner were about 3 feet in the side, and they were liable to the air-bubbles, knots, and striæ so frequent in common window-glass. All these disadvantages disappeared with the invention of the casting process which is now in use. ABRAHAM THEVART devised this bold method, as DUMAS terms it, and put it in practice at Paris in 1685. It was the same artist who founded in 1691 the celebrated manufactory of St. Gobain in Picardy.

Composition.—Plate-glass is similar in composition to crown and sheet glass, the only essential bases being lime and soda; but in plate-glass the soda is introduced in somewhat larger proportion. So far as regards the purity of the tint, it would be attended with advantage to substitute potash for the soda; plate-glasses would thus be freed from the greenish or bluish shade which they sometimes present, and, in this case, one might increase the proportion of lime, which is kept comparatively low in plate-glass to avoid devitrification. But soda is preferred to potash for this description of glass, because it imparts a higher degree of fluidity, and because the impurities which it contains are more readily dissipated by the heat; so that the use of soda, though objectionable as tending to colour the glass, facilitates both the fining and casting—two most important advantages in the manufacture. Subjoined is the analysis of a plate-glass :—

	Centesimally.		Oxygen.	
Silica,	75·9	=	39·4	
Alumina,	2·8	=	1·3	
Lime,	3·8	=	1·0	= 6·7
Soda,	17·5	=	4·4	
	100·0			

The preceding analysis is elementary and theoretical; the subjoined practical recipes are given in KNAPP's "Technology:"—

Composition used at St. Gobain.	Composition according to BASTENAIRE.
100 lbs. pure sand from Senlis.	100 lbs. white sand.
35 lbs. pure salts of soda.	60 lbs. salts of soda.
5 lbs. lime, crumbled.	13 lbs. carbonate of lime.
100 lbs. broken glass.	100 lbs. broken glass.
Decoloring matters.	1 lb. peroxide manganese.
	0·5 lbs. smalt.

The following proportions, which have been used in England, are said to produce a superior quality of plate-glass :—

	Parts.
Lynn sand, well washed and dried,	720
Alkaline salt, containing 40 per cent. of soda,	450
Lime, slaked and sifted,	80
Nitre,	25
Broken plate-glass,	425

These quantities produce one pot of *metal*, which yields 1200 lbs. of glass.

The object aimed at, in making mirrors, is to give the most perfect transparency to them, and to destroy the slightest traces of coloration. With this view, not only must the metal or melted glass be thoroughly fused, but the original materials must be selected with very great care. The sands which enter into the composition should be very white and fine. In default of suitable sand, soft sandstone, white and well pulverized, is used. Flint and quartz, calcined and reduced to powder, are excellent materials for the purpose. Particular care must be taken in the choice and treatment of the soda, to avoid, as far as possible, the green tint which is peculiar to glass formed with this alkali, and which the thickness of the plate-glass betrays. It might be possible to counteract this evil to a certain extent by a perfect fining or purification of the soda, and by replacing part of it with potash, to the amount of about one-fifth. If plate-glass were formed with potash alone, instead of soda, it is to be feared that a glass necessarily so rich in alkali would be hygrometrical, and would partake too much of the nature of soluble glass. Even the small proportion of potash which, in the shape of nitre, usually enters into the composition of French plate-glass, is found to give it a dampness, so that when two of these are kept together for any length of time, they can scarcely be separated. VARLEY stated at a meeting of the Society of Arts, that he was once shown some very large glasses by a London manufacturer, which were beautifully clear, but appeared to be covered with steam, and this, when wiped off, appeared again. The manufacturer had applied to FARADAY in hopes of learning how to cure this imperfection. On examining these glasses with a magnifier, the apparent steam was found to consist of very minute but long crystals, whose shape indicated nitre, showing that so much potash was used in the manufacture of the glass that it exuded. Now, repeated washings, which with 8 or 10 feet glasses is a serious labour, might much lessen the exudable matter; but the glass would thus become porous all over, and its power of transmitting or reflecting light would be diminished. What was still worse was, that

such glass could never be wiped so as to remain clean, for the wiping filled up the pores with what should have been quite removed. This began again to exude in minute gummy dots, which continued to enlarge, and on again wiping, smeared the surface, rendering it difficult to clean. Soda is prone to dry and lose its water of crystallization; potash, on the contrary, attracts moisture, and becomes liquid. Hence it would seem that soda must make the more durable glass, besides fulfilling the important conditions of rendering the vitreous composition more fusible and more easy to fine. The latter advantages arise from the fact, that the gall or sandiver of the soda-glass, consisting of sulphate of soda and chloride of sodium, is more volatile than potash-gall, and is hence more readily got rid of from the open pots in which the glass is fused.

Flint-Glass.—This compound is frequently termed *crystal*, from its great resemblance to rock-crystal. It is chiefly manufactured into articles of domestic use and ornament, such as tumblers, decanters, wine-glasses, vases, drops for chandeliers, &c. In consequence of its great transparency and high refractive power, it is also formed into lenses for optical instruments. On the Continent the term flint-glass is almost exclusively applied to glass which is expressly manufactured for the latter purpose, and *crystal* is employed as the more comprehensive designation for glass containing lead, of which flint or optical glass is regarded as a variety. In this country, flint-glass and crystal are used as synonymous terms, and that particular variety of this description of glass which is manufactured for optical purposes is termed *optical glass*.

Flint-glass is so called from the circumstance that, formerly, flints calcined and ground were employed in the manufacture as the source of the silica; but for many years past Isle of Wight, Lynn, or Reigate sands have been substituted. These sands are not only more free from iron, but less expensive in the preparation than flints, when washed and calcined. It is more properly termed lead glass, since it is the presence of this metal which distinguishes flint-glass or crystal from the different varieties of glass already mentioned. It is also distinguished from English crown and plate-glass by the use of potash, instead of soda, in the manufacture.

This beautiful variety of glass is admitted on all hands to be of English origin. Its invention was a natural and almost necessary consequence of the use of coal in the English manufactories—a usage which goes back to a very remote epoch. To prepare white glass in an open pot, with coal as fuel, is a problem which admits of being solved at the present day, but which could not be so at an early period. To protect the glass from the contact of the smoke which blackened it, it was necessary to convert the common pot into a retort with a short neck, which presented its mouth outside the furnace. But under this condition the temperature of vitrification of ordinary glasses could not be attained without increasing beyond measure the proportion of alkali. It was essential, therefore, to find the means of increasing the fusibility of the glass, without rendering it deliquescent; and this was accomplished by means of a suitable addition of protoxide of lead. The beauty of the product soon assigned it a high rank among the different varieties of glass, and the manufacture of it was not long in extending even into countries where coal is not used. But in these localities the manufacture could be conducted in common pots, taking care to manage the wood fire so as to avoid all production of smoke, and modifying slightly the proportion of the substances employed.

Flint-glass, however, is not entirely a modern invention, or, at least, if it was necessary to re-invent it, it is certain that it was known at a very remote epoch. This is demonstrated by the analysis of the ancient glass known as *Virgil's mirror*, an operation performed in 1817 by M. Fougeroux de Bondaroy. This mirror, weighing 30 lbs., polished on both faces, transparent, but coloured a yellowish green, contained at least half its weight of oxide of lead, and exhibited, moreover, all the characters of crystal. It had been preserved in the treasury of Saint Denis in France from the time of its fabrication, which assigns to its manufacture a date long anterior to the discovery of modern crystal. It is evident, indeed, that the name applied to the mirror is not correct, and proves nothing—that it did not belong to Virgil, and that it could not claim an antiquity so remote. This article only proves that the method of making lead-glass had been long known, and that the processes of the manufacture must have been well understood, since at that time a mirror could be formed of a size which would be deemed remarkable even at this day, and that the secret had been lost during a long succession of years. It may, however, be affirmed that the colourless crystal or lead glass of the present day is entirely of modern invention. It is very natural to suppose that the method of making a coloured crystal like Virgil's mirror might be known to many mediæval chemists, without assuming that they equally knew how to prepare a pure and colourless glass like that now manufactured.

The formulæ expressing the constitution of different varieties of flint-glass are as follows:—

London crystal, Faraday,..... $K_2O(SiO_2)_3 + Pb_2O(SiO_2)_3$.
" Optical, Berthier, $2(K_2O(SiO_2)_4) + 3(Pb_2O(SiO_2)_4)$.
Newcastle, Berthier,..... $2,K_2O(SiO_2)_3) + 3,Pb_2O(SiO_2)_3$.
Belgian, Berthier,..... $K_2O(SiO_2)_4 + 2(Pb_2O(SiO_2)_4)$.

Composition and Properties of Flint-Glass.—From these formulæ it may be observed that the proportions of the three essential constituents, namely, silica, potash, and oxide of lead, vary very much; in fact, they depend on whether the melting furnace is heated with wood or coal. In the latter case the proportion of oxide of lead is increased.

Many metallic oxides are capable of combining with silicic acid, and thus furnishing silicates which readily mix with alkaline silicates; but almost all these are coloured. Till lately, the protoxide of lead and the oxide of bismuth were regarded as the only oxides capable of yielding silicates with little colour, and consequently colourless glasses, by their mixture with the silicate of potash in a proper pro-

portion; but a *glass of zinc*, which had a very pleasing and white appearance, and appeared suitable for achromatic purposes, was the subject of a reward at the Great Exhibition of 1851. This glass is of greater specific gravity, and is as pellucid as lead-glass. On the other hand, the oxide of bismuth is much dearer than that of lead, and hitherto the latter has been alone employed in the manufacture of common crystal.

Crystal or flint-glass well prepared is almost without colour. Its specific gravity ranges between 2·9 and 3·255, according as the lead is in the state of tri- or tetrasilicate. It is more transparent, more brilliant, and heavier than plate or window-glass. The absence of colour depends on the lead silicate, which is yellow, being combined with a due amount of potassium silicate. It excels the fine Bohemian crown-glass in refractive power and easy fusibility, although the latter is harder and more completely colourless. Flint-glass, of not less than the usual density of 3·200, well polished by the lapidary, is considered the nearest approach to the diamond. It owes its brilliancy and high density to the silicate of lead. The proportion of potassium silicate is therefore reduced as low as possible, without suffering the yellow tinge due to the lead silicate to appear, when flint-glass, or "strass," as it is called, is made for jewellers. The composition of a strass analyzed by DUMAS corresponded with the formula, $K_2O(SiO_2)_2 + 3(Pb_2O(SiO_2))_2$. The silicate of lead is much softer than the alkaline silicates. In too large quantity, therefore, it renders the glass easy to scratch by the slightest friction, so that it could not be employed for most of the articles of domestic use into which it is fashioned. Moreover, this addition rendering it both heavier and more costly in the manufacture, would be at least useless, even if it were not absolutely prejudicial, for the reasons already mentioned. It is a common mistake to suppose that great density or *weight* is an advantage in crystal for articles of common use. It is, on the contrary, as DUMAS justly remarks, a real inconvenience, and in the most favourable view can only be considered as a ready means of showing that the crystal or flint-glass contains enough of silicate of lead to impart to it those qualities which give it its peculiar value, and render it preferable to other glasses for certain purposes.

As lead affords the only metallic oxide which is usually employed in the manufacture of flint-glass, so potash is the only alkali which can be successfully associated with that ingredient to yield a colourless crystal. The silicate of soda always communicates a blue or green tinge, which would become more perceptible and disagreeable in the thick articles usually manufactured of crystal. If this thickness were much reduced, the silicate of soda might, so far as colour is concerned, be used in the manufacture; but as crystal vessels are generally intended to receive mouldings or cut ornaments, they do not admit of being made thin in the sides. The annealing, also, would become a difficult operation in vessels of considerable size without a proportionate thickness. Crystal is so fusible that it is not easy to prevent such articles from sinking in, or collapsing, during the annealing. This kind of glass is, therefore, almost exclusively confined to the manufacture of thick articles; and hence it is only the colourless silicates that can be used—that is to say, those of lead, or zinc, and potash. The following practical recipes are given by BASTENAIRE for a good common flint-glass, the one with coal, and the other with wood as fuel:—

	With coal as fuel.	With wood as fuel.
	Lbs.	Lbs.
Sand—washed and calcined,	100	100
Minium,	70	45
Purified potash,	30	35

In addition to these, cullet or broken glass is added at discretion, and saltpetre or arsenic is used as a decoloring material. It will be seen that, when coal is used, the sand, red lead, and potash are nearly in the proportions of 3 : 2 : 1; but that, when the composition is fused in open pots, with wood fuel, the proportion of the red lead is much diminished. The following composition, in which the above-mentioned proportions of the principal ingredients are exactly adhered to, is given by APSLEY PELLAT, as yielding a highly pellucid and transparent flint-glass:—

Carbonate of potash,	1 cwt.
Red lead, or litharge,	2 cwt.
Sand—washed and burnt,	3 cwt.
Saltpetre	14 to 28 lbs.
Oxide of manganese,	4 to 12 ozs.
Cullet, or broken glass, *ad libitum*.	

FLINT-GLASS—LOYSEL.

	Parts.
White sand,	100
Red lead	80 to 85
Pearl ash,	35 to 40
Nitre,	2 to 3
Manganese,	0·5

FLINT-GLASS—AIKEN.

	Parts.
White sand,	100
Pearl ash,	40
Red lead,	35
Nitre,	13
Manganese,	0·5

FLINT-GLASS.

	Parts.
Sand,	100
Carbonate of potash,	50
Chalk	20
Saltpetre,	1·8
Arsenious acid,	1·8
Manganese,	0·1

The following proportions, in use in various works, show the great diversity in practice existing:—

	Parts.
Sand,	100
Carbonate of potash,	60
Saltpetre,	8
Arsenious acid,	0·4
Manganese,	0·5

Sand,	100
Red lead,	40
Carbonate of potash,	33
Saltpetre,	16
Manganese,	0·5

	Parts.
Sand,	100
Carbonate of potash,	33
Red lead,	30
Saltpetre,	10
Manganese,	0·15

Sand,	100
Red lead,	60
Carbonate of potash,	24
Saltpetre,	6
Arsenious acid,	trace.
Manganese,	trace.

PLATE-GLASS.

	Parts.
Very white sand,	100
Carbonate of soda,	33
Chalk,	14
Manganese,	0·75
Cullet,	100

PLATE-GLASS.

	Parts.
Very white sand,	100
Carbonate of soda,	62
Quick lime,	11
Saltpetre,	4
Cullet,	60

FOREIGN LOOKING-GLASS.

	Parts.
White sand,	100
Carbonate of soda,	30
Lime,	14
Cullet,	100
Manganese,	0·5

Dumas affirms that a finer and more durable product is obtained by reducing the amount of alkali; thus, for 300 parts of sand and 200 of minium, 90 to 95 parts of purified carbonate of potash, instead of 100, will yield a better result when the furnace draws well—in winter, for example. But in summer, the preceding proportions must be used, or the following French recipe:—

	Parts.
Pure sand,	300
Minium,	215
Purified carbonate of potash,	110
Nitrate of potash,	10
Borax,	12

Borax must be used with great caution, as an excess leads to exfoliation of the glass.

It has been stated that when open pots are used, as on the Continent, with wood fuel, the proportion of minium may be reduced. This arises from the circumstance that the oxide of lead, being an active flux, is less necessary for the fusion in uncovered pots, which admit of the direct action of the heat on the contained mixture or metal. However, the use of the three essential ingredients in the ordinary proportion of three, two, and one, is in all cases a safe one. It is chiefly for economy that the minium is reduced in amount, when the heating power of the furnace is sufficient to permit the reduction. On the other hand, if the minium be too much reduced, the beauty of the product will suffer. The lowest proportion of this ingredient which can be used with safety is shown in the following composition, which yields a good crystal:—

	Parts.
Sand,	300
Minium,	180
Purified carbonate of potash,	120
Cullet,	300
Arsenious acid,	0·15
Oxide of manganese,	0·60

The mere due proportioning of the materials for flint-glass is not sufficient—the utmost attention must be given to have them in a state of purity. The silica or sand should be very white, and absolutely free from colouring oxides, as those of iron or manganese. Some manufacturers cleanse the sand by hand-washing, and others have machines. To render the Isle of Wight sand fit for making flint and other compound glasses—that is to say, to cleanse it from chalk and other impurities, by which it loses about one-fifth of its original bulk, requires about eight waters; it is afterwards passed through a heated arch, called a *calker*, and thoroughly dried, or burnt, at the discretion of the operator; and then sifted through a lawn-sieve, to separate the larger grains and pieces of coal or coke. Dumas recommends that the sands be washed with dilute hydrochloric acid, to remove from them any traces of oxide of iron or of manganese.

The carbonate of potash also requires a preliminary purification, which is easily effected by dissolving it in water, decanting the quite clear solution, and evaporating the liquor. All the colouring oxides are deposited, and by the evaporation carbonate of potash is obtained, mixed with other salts, but at least quite free from oxides of iron or of manganese. If the nitrate of potash were low in price, it might be employed to replace the carbonate.

The protoxide of lead, or litharge of commerce, is almost always impure. It contains oxides of copper, of iron, or of manganese, in too great quantity, in most cases, to admit of its making a colourless flint-glass. An oxide of lead is therefore expressly manufactured for the making of crystal. In general, a very pure lead is selected for this purpose, which is carefully oxidized, to avoid introducing into it foreign and injurious matters. It is the practice to carry the oxidation of the lead to the state of *minium*. Not that the crystal contains red lead; the latter loses by the action of the heat a portion of its oxygen, and passes again to the state of protoxide which alone forms part of the glass. But it is advantageous, and probably even indispensable, to furnish to the mixture which is to produce the flint-glass a body capable of yielding oxygen at the beginning of the fusion.

It has been supposed that this disengagement of oxygen was necessary to produce in the glass the agitation which prevents this product from separating itself in layers of different densities. But Dumas observes that the decomposition of the minium must be concluded long before the fusion is effected. The oxygen which the minium disengages has very probably for its object to burn an organic matter analogous to ulmin, which is found in large quantity in the crude salt; a matter which is decomposed in part, calcining this last to make potash of it, but which is still found in the potassas of commerce in notable quantity. This matter, put in contact with the protoxide, would reduce it to the metallic state, and would colour the crystal; whereas, being burned by the oxygen of the minium, it disappears without leaving a trace of its existence.

It is evident that the same result would be arrived

at by using nitrate of potash instead of the carbonate, and that the minium might be replaced by pure litharge, or protoxide of lead. In point of fact, the small quantity of saltpetre which is usually added exerts a beneficial effect, by increasing the proportion of oxygen, and assisting to drive off the globules of air in the liquid glass. This salt, when the price admits of its application, is at once a pure and a purifying material. A few ounces of manganese are employed to neutralize the greenish tint produced by the presence of iron or other impurities, and with this view the binoxide (MnO_2) must be used in the purest state.

Optical Glass.—There are two kinds of optical glass—flint and crown—which, having different refractive and dispersive powers, may be so combined in the object-glass of a telescope that, while the rays are brought to a focus, the greater dispersion of the flint lens may be corrected by the less dispersive power of the crown—the one being negative, the other positive. Hence, by their combination, the lenses achromatize each other, or transmit colourless light. The celebrated Dollond, in 1753, aided by the co-operation of Euler, and of Klingenstierna the Swedish mathematician, succeeded, after many experiments, in discovering the due proportions of the curvatures of the two lenses; but still two important problems remained to be solved—the best chemical constitution of the glasses, and how to obtain them sufficiently free from the defects of ordinary glass to be adapted for optical instruments. It is this last question which presents the greatest difficulty. Purity, unchangeableness of colour, transparency, and a certain degree of refractive power, may be obtained; but perfect uniformity in the structure of the glass, so as to render its composition absolutely homogeneous throughout, is much more difficult to be accomplished; and this is precisely the quality which is admitted to be the most indispensable for good optical glass. The difficulty arises chiefly from the difference in specific gravity of the different constituents of the metal. Some melt at a lower temperature than others; some evaporate or are decomposed in a heat required for the fusion of others; and different substances cool at different temperatures. Hence arise discoloration, threads, striæ, irregular crystallization, causing irregular refraction, and all the usual faults observable, more or less, in every description of glass.

It seems to be now generally admitted that there are more impediments in fabricating crown-glass lenses of large size than in making good ones of crystal or flint-glass. The former requires a higher temperature, and by adding alkali to increase the facility of fusion, it becomes more liable to attract humidity, or, as it is technically termed, to sweat. On the other hand, by rendering it too hard, the risk is incurred of crystallization and imperfect vitrification in cooling.

The problem of the constant and regular manufacture of good optical flint-glass was solved by M. Guinand, a workman in the clock and watch trade, near Neufchatel, who succeeded in producing masses of flint-glass capable of furnishing objectives of 9 inches—a size previously unknown. Guinand kept the process a secret, except from M. Utzschneider and the celebrated M. Frauenhofer, who proposed to him to join them in their establishment at Munich. This offer Guinand accepted, and the process was successfully worked by them for several years without any one being able to discover it. After their deaths, one of Guinand's sons being in possession of his father's method, continued the manufacture of optical glass in the environs of Neufchatel. Guinand's heavy glass of the specific gravity 3·616 is made from:—

	Parts.
Ground quartz,	100
Red lead,	100
Carbonate of potash,	35
Saltpetre,	2 to 4

The other son formed an association with Bontemps, one of the directors of the glass-work of Choisy-le-Roi, but the experiments which were made by them conjointly at that establishment did not succeed. The treaty was therefore broken; but Bontemps and his co-director, Thibeaudeau, satisfied of the correctness of the principle, if properly applied, continued their experiments without excluding Guinand; and ultimately, in 1828, they succeeded in producing good optical glass in discs of from 12 to 14 inches, and a large quantity of small sizes. From that time the manufacture has been established on a regular system.

In 1848 Bontemps was induced, in consequence of difficulties arising from the political state of the country, to retire from his position at Choisy-le-Roi, and to accept the invitation of Messrs. Chance Brothers & Co. to unite with them in attempting to improve the quality of this important branch of manufacture. How far they have succeeded may be judged of from the fact, that they have produced discs of flint-glass 29 inches in diameter, weighing 2 cwts., and of crown-glass up to 20 inches. These discs are pure in colour, good in structure, and exempt from those defects which tend to polarization of light. Bontemps' proportions for optical glass are as follows:—

FOR FLINT-GLASS.

Sand,	43·5
Red lead,	43·5
Carbonate of potash,	10·0
Nitrate of potash,	3·0
	100·0

FOR CROWN-GLASS.

Sand,	60
Carbonate of soda,	25
Carbonate of lime,	14
Arsenic,	1
	100

It will be observed that optical flint-glass is chiefly distinguished by the large proportion of lead which enters into its composition. The essential point in the manufacture, however, consists in the constant stirring of the metal during the melting and fusing.

The superiority of Guinand's plan is considered not to have been in the novelty of the materials or proportions, but in carefully agitating the liquid glass while at the highest point of fusion, *then cooling down the entire contents of the pot in a mass*, and when annealed and cool separating unstriated portions by cleavage. It is worthy of remark that some time before Guinand's death a commission of the Astronomical Society of London, composed of Herschel, Faraday, Dollond, and Roget, having been instructed to conduct an inquiry into the manufacture of flint-glass for optical purposes, arrived at the result that the necessary improvement was chiefly mechanical, not chemical, and that freedom from striæ could only be obtained by a constant agitation of the mixture. Faraday, who took the lead in the inquiry, both in his own laboratory and at the glass-works of Messrs. Pellatt, changed, however, the composition, as well as the principle of fabrication, and produced a borate of lead of remarkable purity. This substance, known as Faraday's heavy glass, which has proved so important in experiments connected with the polarization of light by magnetic action, is composed of the following ingredients:—

Protoxide of lead,	104
Silicate of lead,	24
Dry boracic acid,	25

This glass required but a red heat for fusion, thereby, as Pellatt remarks, offering facilities for minute agitating operations. It was found, however, not to be durable, and therefore not calculated for application to optical purposes or general use. The common process for making optical glass is as follows:—A ladle, in the form of a sugar-loaf, about 5 inches in diameter and 7 inches deep, is dipped carefully into the metal, which has been previously skimmed; when filled, it is taken out of the pot, and suffered to get partially cool. To the large end of the sugar-loaf-shaped piece of glass thus produced, a glass-blowing iron with a hollow disc is welded, and placed to the opening or mouth of the pot for reheating; when sufficiently soft, it is blown into a muff; the end furthest from the blowing-iron is cut off, the cylinder is flattened into pieces or plates of 14 inches long, 10 inches wide, and about half an inch thick, and annealed; in which state the plates are sent to the optician for cutting and grinding.

Working Operations.—The tools represented by Blancourt, in his work "On the Art of Glass," which was printed at London in 1699, are almost precisely the same as those now in use; and the author's account of their mode of working might almost be taken.

The most important is the "pipe," on the end of which the glass is taken up by the workman, and blown into spheres or bulbs, to be subsequently shaped into different forms, as will be afterwards described. A section of this indispensable instrument is shown in Fig. 21. It is simply a tube, composed of wrought-iron, 4 to 5 feet long, 1 inch thick, and about one quarter to 1 inch in the bore. It is provided with a knob at each end, the one of which, *a*, serves as a mouth-piece, whilst to the other, *b*, the melted glass is attached. The upper portion is surrounded by a wooden cover, *c*, to protect the hands of the workman from the heat of the metal. A companion to this instrument is a solid iron rod, known as the *pontil* or *ponty*, which serves to receive the glass after it is blown on the pipe. The *spring-tool*, A (Fig. 22), is a species of tongs for laying hold of half-formed handles, and for seizing the glass while making. The *pucellas*, B, have prongs resembling the cutting part of shears, but blunt, and are used for rubbing the outside of solid or hollow glass, and pressing it into smaller diameter, at the

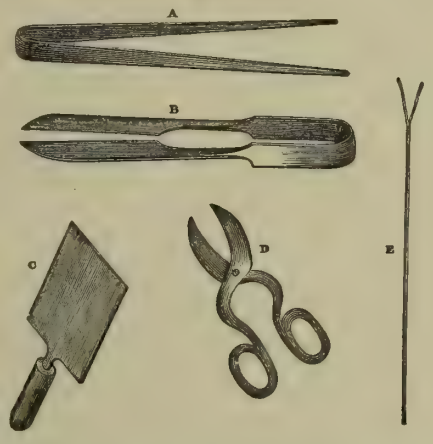
Fig. 21.



same time elongating the parts by rotation. The battledore, C, is made of wood, and is used for flattening the glass when necessary The shears, D, are strong scissors for cutting and shaping the edges and handles of glass vessels while in a soft state. The fork, E, is employed for carrying the finished articles to the annealing oven.

An important part of the glass-blower's furniture is the *marver*, which consists of an iron plate or slab, resting on a stone or on wooden supports, and having a polished surface, on which the mass of glass that has been gathered at the end of the blowing tube is rolled, to give it a symmetrical form. The term

Fig. 22.



marver is derived from the French *marbre*, a marble slab being formerly used. The *glass-maker's chair* is a flat seat of wood, about 10 inches wide, each end of which is fixed to a frame connected with four legs and two inclined arms, upon which is screwed an edging of wrought-iron for rolling the blowing tube with the hot glass backwards and forwards with the left hand, while the required form is given to the glass with the pucellas held in the right. Continual rotation of the melted mass is the principal point to be attended to in most of the glass-blower's operations.

Bottle-Glass.—The melting-furnace for bottle-glass commonly contains only six pots. These are about

3 feet in height, and nearly the same in diameter. They are filled almost to the edges; and when the matter has sunk down, and is converted into a glass, more of the composition is put into the pots, and the fire is urged. The meltings are rapid; for as most of the bottle-glass compositions furnish but little glass-gall, no time is lost in fining. The process lasts from seven to eight hours, and when it is concluded the fire is slackened, that the glass may thicken to the point suitable for working it. For this purpose the fire-place is heaped up with small coal, draughts are intercepted as much as possible, and care is taken not to touch the fire during the working of the glass, lest the combustion should be re-excited.

As soon as the working holes are opened, the surface of the glass is cleared from sandiver or glass-gall. By dipping the previously warmed pipe into the pot, a little glass remains attached to the end; after turning this in the air before the hole until it is cooled, and blowing slightly into it to render it hollow, a fresh layer of glass may be attached to it in the pot; to this a third is added in the same manner, until the ball at the end of the pipe has accumulated to a sufficient size. That this ball may become uniformly tractable in the subsequent forming, it is held by the workman in the flame of the furnace through the working hole; it is then brought into one of the round concavities of the "marver," which is wetted or moistened when used. Here the ball gradually assumes the form of a thick hollow globe, or rather pear-shaped vessel.

Thus far advanced, the glass has again become cool, and is re-heated by insertion into the working hole, in such a manner that the front part receives the chief portion of the heat, and becomes the softer. The pear-shaped vessel is now lengthened by the blower, and its form is made somewhat to resemble that of a bottle by a threefold operation: by blowing into the tube with greater force, swinging it backwards and forwards in the manner of a pendulum, and by a simultaneous constant rotary motion of the pipe round its axis. As soon as the vessel is of the right size it is inserted in a cylindrical hollow block of wood or iron, placed at the side of the workman who is blowing the pear-shaped vessel; and by blowing forcibly into the tube the glass is pressed firmly against the sides of the mould, whilst, by a kind of jerking motion, the neck is drawn out to the proper length. The unfinished bottle, which as yet has no bottom or mouth, is again warmed in the working hole in such a manner that the lower part only is heated, whilst the other part remains comparatively cool. In the meantime another workman or a boy has attached a small quantity of glass to the ponty or pontil, which is also kept hot in the working hole. Both workmen now stand opposite to each other; and whilst the pipe and ponty are kept constantly turning, the latter is forcible pressed against the middle of the lower part of the bottle, which is thus forced inwards, and an even edge is produced, upon which the bottle may stand steadily. The bottle remains for some moments between the two instruments, until, by the application of cold iron or a drop of water, the neck can be separated from the pipe. This is an operation of constant recurrence in the glass-house, and is effected by a sudden change of temperature produced at the point of separation in the hardened glass, either by the cold application of a drop of water, or by the powerful heat of a red-hot iron, or thread of liquid glass from the pot. The point of separation sometimes requires to be re-heated, to cause it to fly on the application of cold water. The bottle is now supported by the ponty, so that the neck can be warmed, and the sharp edges melted round without softening the other parts. A rotating motion is then given to the red-hot neck, the pipe being rolled backwards and forwards upon the knees of the workman. The bottle then revolves upon the axis, and it is only necessary to press the pucellas, or an iron instrument like a turning chisel, against the mouth to widen or reduce it to any required dimensions; the rim for strengthening the neck is formed from a drop of glass taken from the pot by the edge of the flask, and wrapped round the mouth in the form of a thick thread. The bottle, which is now finished, is immediately carried on the ponty-rod to the annealing-oven by a boy, pushed into its proper place, and the ponty-rod is finally detached from the bottom of the bottle by a sudden sharp jerk. The place where the ponty was attached is perceptible in every bottle blown in this manner, by the sharp edges where the fracture occurred.

Large round bottles are blown without the use of a mould, and when of a very great size, like the carboys for sulphuric acid, the aid of steam is called in, by spirting about an ounce of water into the interior, and holding the mouth of the pipe with the thumb.

Tube-drawing.—The operation of "tube-drawing" depends on the singular fact, that when a hollow lump of glass, for instance a globe, is drawn out whilst hot, the cavity in the interior is always preserved, even when the glass is drawn out to the tenuity of the finest thread.

Whilst one man collects the necessary quantity of glass on his pipe, and blows this out to a very massive globe, preserving a uniform thickness of the sides as much as possible—the other attaches a drop of glass to a ponty-rod, and warms it on the fire by the side of the globe. Both instruments are then removed from the fire at once, and the ponty-rod is pushed forcibly against the globe in such a manner as to form exactly a straight line with the pipe. This being accomplished, one of the workmen retires backwards as quickly as possible, to the distance of 50, 60, or 100 feet. In this operation the globe at first shrinks, and forms the commencement of the tube, which soon cools, and does not diminish in thickness, whilst the mass of glass is spun out by the constant drawing from the warm end. Continual rotation of the pipe and ponty-rod is necessary, or the part of the tube nearest the ground would cool quickest, and the tube thus assume an irregular form. This, however, does not prevent the tube, in conse-

quence of its great length, from sinking in the middle like a stretched rope, and it becomes, consequently, thicker at the two ends. The curve in the tube is, however, remedied by placing it on a ladder before it has become perfectly set; it then straightens, and is cut into lengths of 4 or 6 feet each, by taking hold of it with a cold pair of tongs. Tubes cool very uniformly, in consequence of their small amount of metal, and they are, therefore, not placed in the annealing oven. Lastly, the bore of the tube is dependent upon the length to which a given mass of glass is stretched, or, the length being the same, upon the mass of glass; the stoutness of the tube is, however, determined by the thickness of the sides of the original globe, as the relation between the thickness of the sides and the bore is not altered by drawing. Wide, thin tubes must therefore be drawn out of a large thin globe, and *vice versâ:* it is necessary, however, whilst the tubes are drawing to blow into them, that the sides may not sink in.

English Crown-Glass.—Assuming one or other of the mixtures or compositions already given to be melted in the crown-glass pot, upon the surface of the melted glass is a ring of fire-clay, which, when the materials were thrown in, lay at the bottom of the pot, and after the completion of the melting, found its way upwards. This ring, floating in the centre of the pot, prevents the exterior surface of the melted glass, which becomes stiff and stringy during the long period of working, from mingling with the interior or hotter surface, which thus remains throughout of a suitable consistency. The labour also of the skimmer is considerebly diminished by the ring, which, limiting the space from which the glass is drawn, limits also the space which it is necessary to cleanse, and any bubbles or impurities in the glass have a tendency to attach themselves to the ring.

The metal, or melted glass, having been brought. by the gradual cooling of the furnace, from a state of complete fluidity to a consistence capable of being worked, the *gatherer* dips the end of his pipe, or hollow rod of iron, into the pot inside the ring, and twirling it round its axis, to equalize the thickness of the gathering, collects upon the end, or nose, as it is technically called, a pear-shaped lump of glass. Resting his pipe upon a stand, or "horse," he turns it gently round, and allows the surface of the lump to cool, to fit it for a second gathering. So much glass is collected in this way, in successive layers, as will form a disc or table of about 9 lbs. weight. The lump completed, the gatherer, having cooled his pipe under a trough of water, that he may handle it at any point, proceeds to roll the glass upon the marver, or metallic bed, until it assumes a conical form, the apex of the cone forming what is termed the *bullion-point.* A boy now blows down the pipe while it is still being turned by the gatherer on the marver, and expands the glass into a small globe. Having been heated, it is blown again, and assumes the shape of a Florence flask. Again heated, it is now expanded by the blower into a large globe. During this expansion it is important to keep the bullion-point exactly in the position which it previously occupied, in a line with the axis of the pipe. To effect this, the blower rests his pipe upon an iron support, and while he blows down the pipe and turns it round at the same time, a boy holds against the bullion-point a piece of iron terminating in a small cup. Again presented to the fire, by the peculiar manipulation of the workman, and the peculiar direction of the flame upon it, the front of the globe is flattened, the possibility of the globe collapsing during this operation being prevented by its rapid revolution round its axis. The pipe is laid horizontally upon an iron rest, and a man approaches, having in his hand a ponty, tipped with a lump of molten glass. Pressing this lump upon an iron point, so as to give it the form of a little cup, he fits it, when thus shaped, on to the bullion-point, to which it soon becomes firmly attached. The lump thus formed is called the *bull's eye,* or bullion of the developed plate. The incision of a piece of cold iron in the glass round the nose of the pipe, and a smart blow, soon detaches the pipe, leaving a corresponding hole in the flattened sphere, at a point exactly opposite the attachment of the ponty. The blowing pipe thus removed, and carrying with it a piece of glass, is allowed to lie idle a few minutes, till the glass adhering to it has cracked off; it is then warmed, and carried back to the pot to repeat its course in a similar operation.

The open projecting end of the piece, which was next the now detached pipe, is called the nose, and gives its name to the furnace or nose-hole, where this nose is, on account of its thickness, heated almost to melting, with a view to the next operation. It is now that the glass undergoes its last treatment in the hands of a man who, with a veil before his face, stands in front of a huge circle of flame, termed the "flashing furnace," into which he thrusts his piece, rapidly, meanwhile, revolving his ponty. The nose of the piece, or hole caused by the removal of the blowing pipe, enlarges, the parts around cannot resist the tendency, the opening grows larger and larger, for a moment is caught a glimpse of a circle with a double rim; the next moment a thin transparent circular plate of glass is whirling round, which, but a few minutes before, was lying in the glass-pot, an indistinguishable portion of the molten glass. The sound of the final opening of the piece has been compared to that produced by quickly expanding a wet umbrella. Still whirling, the "table," as it is now called, is carried off, laid flat upon a support called a whimsey, detached by shears, or otherwise, from the ponty, lifted into the annealing kiln upon a fork, and piled upon its edge against the preceding table. The weight of so many tables pressing one against another would cause the hindermost to bend, but this is prevented by the intervention of iron frames, or drossers, which divide the tables into sets. As the bull's-eye, or centre lump, which the ponty has left behind it, keeps each table from close contact with its neighbours, the air passes freely between them, and the annealing is completed with tolerable rapidity, varying from twenty-four to forty-eight hours, according to the number of tables in the kiln.

Extreme brilliancy of surface is a distinguishing characteristic of this glass, ascribed by some to the influence of the marver, by others to the effect of the flashing-furnace.

It is this brilliancy of surface which has enabled crown-glass to maintain in England its position against the formidable rival which is now to be briefly described.

Cylinder, or Sheet-Glass.—The above method of making window-glass has long been abandoned on the Continent, where the glass is first formed into a spheroid, the ends of which are cut off, so as to form a cylinder open at both extremities; this is then cut lengthwise with shears, or a straight line is traced with a drop of water in the direction of the length of the cylinder, and over the line so traced a red-hot iron is passed, which immediately produces a very uniform crack or fracture along the whole length. The cylinder, thus split up, is then taken to the furnace to be spread or flattened out into a sheet. The glass so manufactured, though formed of the same materials as crown-glass, is coarser in texture, more wavy and dull, but allows of larger sheets being formed, since crown-glass can only be cut up into comparatively small panes, in consequence of its circular form and the central bull's eye.

The process of making British sheet-glass is as follows:—Imagine, as before, a lump of glass collected upon the end of the gatherer's pipe. For the metallic table or marver is now substituted a block of wood, E, Fig. 25, so hollowed out as to allow the lump, when placed upon it, to be expanded by the blower to the diameter ultimately required. The block, during this operation, is sprinkled with water, to prevent the wood from being burnt, and from scratching the glass. In the meantime the lump is slightly distended by blowing (Fig. 23), and is then carried from the block to the blowing furnace, which is accessible through a number of holes or openings, each hole being allotted to a single blower.

The blowing furnace may be either rectangular or circular; it commonly contains from eight to ten pots, and is constructed of refractory bricks of the same earth as that used for the pots. In front of the furnace, Fig. 25, corresponding to each opening, is a stage or frame of wood, erected over a large pit or well about 10 feet deep, and these parallel stages are sufficiently apart to enable each blower to swing his pipe to and fro in a vertical plane, that the glass may run freely out, as the phrase is, to the required length.

C C are the crucibles; D D the planks on which the workmen stand; E E the moulds, beside each of which is a tub of water. When the glass has been sufficiently heated in the blowing furnace, it is brought out, and held over the head while blown, until it assumes by its own weight a flattened form, Fig. 24. It is then swung round in a vertical plane, as well as backwards and forwards, and the blower at the same time, by blowing down the pipe, constantly keeps the lengthening cylinder full of air. Uniformity of substance and of diameter is chiefly secured by the skill of the workman, who, when he finds the metal running out too freely, repeats the operation of holding the cylinder vertically above his head, still keeping it well filled with air. These operations are continued until the cylinder has reached the length required.

Fig. 23.

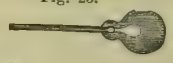
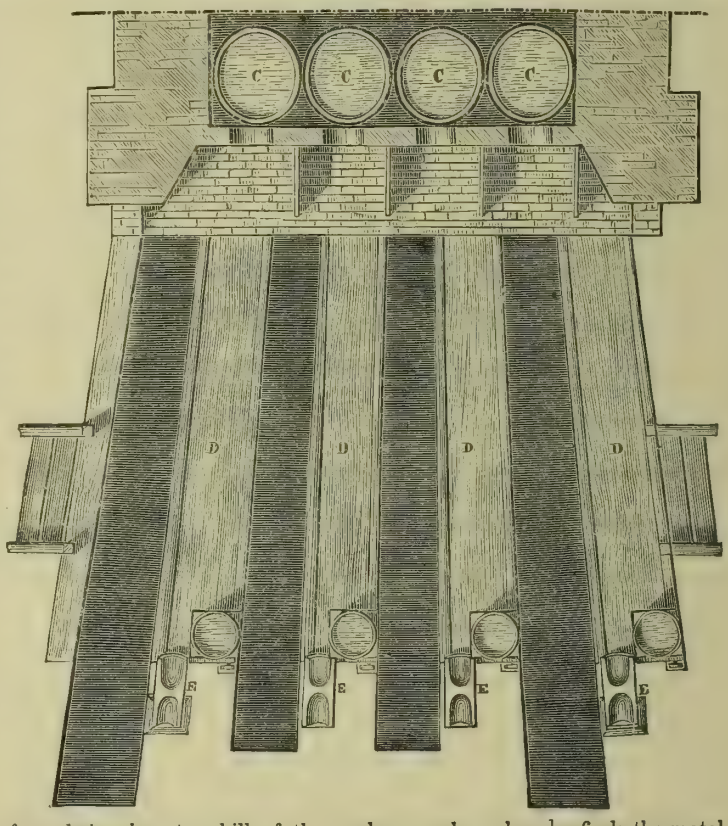


Fig. 24.



Fig. 25.



The next stage of the process is opening the end of the cylinder. The thinner kinds of glass are all opened by submitting this part to the fire, and at the same time forcing in air through the pipe, and stopping up its aperture with the thumb. The air is expanded by the heat of the fire, and bursts open the cylinder at the end, this being the hottest and most yielding part. The thick and uneven margin of the aperture thus formed is trimmed with scissors; and the aperture is then widened out to the full

diameter of the cylinder with the pucellas, and by turning the cylinder to and fro with the opening downwards, until by the centrifugal force, and its own gravity, the yielding glass assumes a uniform diameter with parallel sides.

The ends of the thicker cylinders have an extra mass of hot glass incorporated with the end, which thus becomes the hottest and weakest part, without applying them to the furnace, and the air forced in as before bursts them open. The opening is then enlarged by cutting round it with scissors.

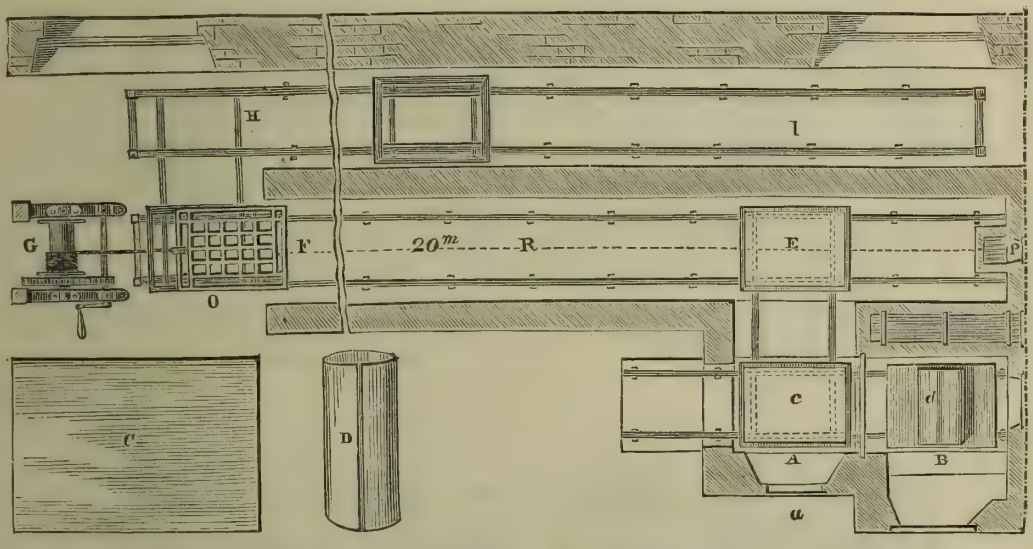
The neck or cap is now removed by supporting the cylinder on a wooden rest, and turning the upper part two or three times in the curve of a bent iron heated to redness, a drop of water allowed to fall on the heated line produces fracture and separation of the cap. Or, the same may be done by wrapping round the end of the cylinder a thread of hot glass, removing the thread, and applying a piece of cold iron to any part which the thread covered.

The cylinder, as it now lies upon the chevalet, is little more in weight than two-thirds of the lump of glass which the gatherer collected on his pipe. The quantity left upon the pipe-nose, with that which formed the cap of the cylinder, are nearly equivalent in weight to one half the cylinder.

The next operation is to split it open along its length. Till of late this was uniformly done by means of red-hot iron and water—a method which is still practised on the Continent; but in the English glass-works it is now effected with greater certainty and regularity by a diamond, which, attached to a long handle, and guided by a wooden rule, is drawn along the inside length of the cylinder.

The use of the diamond in dividing plain surfaces of glass dates from the sixteenth century; but its application to the splitting of the cylinders which had not undergone the process of annealing was introduced by Claudet, the distinguished photographer, then a glass manufacturer.

Fig. 26.



Having been split along its length, the cylinder is introduced into the "flattening furnace." The "flatting-stone," or "spreading-plate," ought, of course, to be perfectly even and smooth, as the soft glass moulds itself to the surface upon which it is flattened by heat. The sandstone of Godstone, in Surrey, has been found to answer well for this plate, which, however, is usually covered with a "lagre" or sheet of glass. The effect of the heat is assisted by spreading out the softened sheet with an iron ruler, introduced through an aperture in the furnace. The flattener now applies another instrument, a 'polissoir," or rod of iron, furnished at the end with a block of wood, and rubs down the waviness into a flat surface. The flattening stone is now moved on wheels to a cooler portion of the furnace, and by the aid of the flattening fork delivers its sheet to another stone, called the cooling stone. From this, when sufficiently stiff, it is again lifted, and then piled generally on its edge, in order to be annealed.

Fig. 26 is the plan of a French annealing and flattening furnace. The cut cylinder, D, is placed in the furnace, B, on a travelling table, *d*; it is then moved into the furnace, A, where it is opened out by means of an iron bar passed through the opening, *a*. The flattened plate, *c*, is then pushed by an iron hook on to the cooling stone, E, and by means of the crane, G, drawn slowly along the gallery, R F. By the time it arrives at the opening, O, the glass is quite cold; it is then removed to the warehouse, whilst the empty carriage is sent along the other line of rails to be returned to the furnace.

Messrs. Chance, instead of at once removing the glass from the flatting to the annealing furnace, and lifting it to the cooling-bed while soft and liable to distortion, flat and cool it by passing it through a succession of decreasing temperatures, so that it is not lifted until it becomes quite stiff and rigid. By this arrangement the workmen can flatten the glass while the annealing is in progress, which could not be

effected by the old method, because the temperature of the flattening kiln must be reduced with that of the annealing kiln, to which it is contiguous, thus leading to the successive heating and cooling of the kiln, and waste both of time and fuel. CHANCE'S flatting and annealing kilns are two circular buildings communicating with each other, and shown in plan and elevation in Figs. 27 and 28. Each of the buildings consists of exterior and interior walls, S, the intervening space being a circular arched vault. In each vault is a cast-iron frame, moving on casters, and capable of being turned round by a winch on the outside, communicating with the shaft and bevel wheels, R R—Fig. 28. The frame, B B, in the flatting kiln carries the flatting stone, *a*, and lagres, A, eight in number, and that in the annealing kiln a number of metallic wires, G, radiating towards the centre of the building, for supporting the sheets of glass. The flatting kiln is heated by the grate, M, and in order that the stones and lagres, which will have cooled during the rotation, may be re-heated and arrive at the position, F, at a proper temperature, a second smaller grate is placed at *b*. If coke be used, a chimney at T will be required, but with wood fuel it will not be needed. Partitions, H, are placed at certain intervals, to prevent the too rapid dissipation of the

Fig. 27.

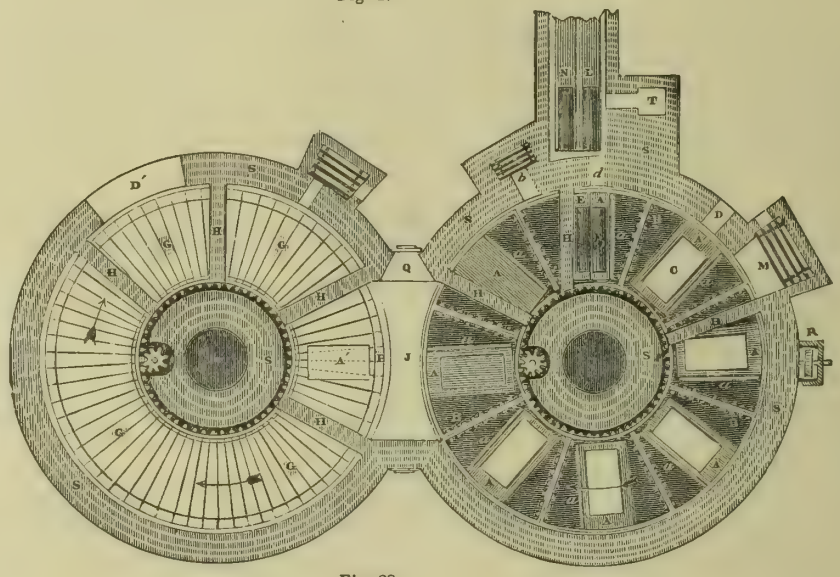
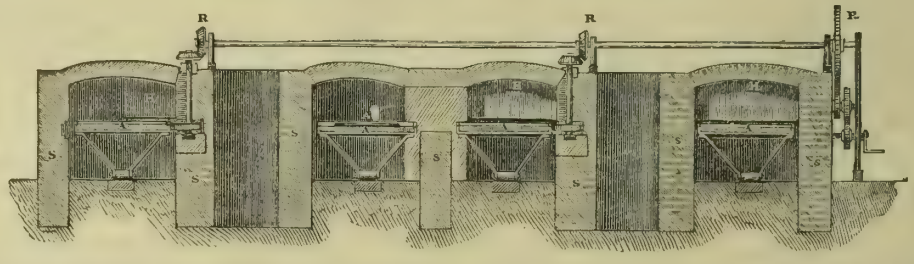
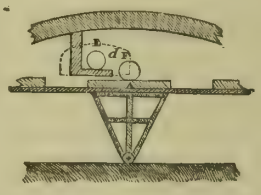


Fig. 28.



heat from those parts where it is most required, and to retard the entrance of cold air through the openings in the external wall. At the bottom of the partitions are spaces to allow the frame, with the stones and glass or the wires and glass to pass below. The space, J, on which the glass is shifted from the lagres to the wires, is lighted by gas. The kiln is worked in the following manner:—The cylinder of glass is first placed in the position, N; then in that of L; thirdly, it is introduced through the external wall, *d*, and placed on a stone, E, suspended over the lagres; it is lastly placed in the position F. on the lagre beneath. To prevent the cylinder rolling off, the stones are provided with a ledge. This part of the kiln is shown separately in Fig. 29. The frame, B, is then turned round till the cylinder of glass occupies the position C, opposite the working hole, D, through which it is then flattened in the ordinary way. From C the glass passes round in the direction shown by the arrow, till it arrives opposite J, when it is shifted to the position A′ on the wires, by the flattener using his instrument through the opening, Q; and after passing through the successive positions, arrives finally opposite D′, where it is drawn out fully annealed.

Fig. 29.



Hartley, of Sunderland, has introduced two improvements in this operation. One consists in making part of the floor of the flatting kiln to consist of a movable stone, about 10 inches in diameter, on which the cylinder is placed; and by causing the stone to revolve on its axis, the cylinder is gradually exposed on all sides to the action of the fire, thereby avoiding the objection to the previous plan, where one side of each cylinder becomes so much hotter than the other. His other improvement consists in making holes, about the eighth of an inch in diameter, all over the flatting-stone.

When this manufacture was new in England, the size usually blown was 36 inches long and 20 wide. The usual size now is 47 inches long by 32 wide, and cylinders are occasionally blown 77 inches long: but large sizes and heavy weights are accomplished only by workmen of the first class. A sheet of this latter size, containing 21 ozs. to the foot, would require for its formation a lump of glass upon the gatherer's pipe of no less than 38 lbs. weight.

The size which sheet-glass can thus reach is obviously a great advantage, and adapts it to many purposes from which the limited dimensions of crown are excluded. It was this glass that covered the Great Exhibition in 1851. A cylinder was blown to cut, as the phrase is, 49 inches by 30; this was subdivided into three panes of 49 inches by 10. About 300,000 of these, extending over 1,000,000 square feet, and weighing upwards of 400 tons, were made in a few weeks, and this without interrupting the ordinary produce of the manufacturers (Messrs. Chance & Co.).

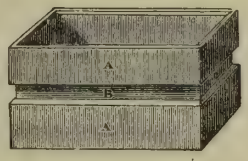
Grinding and Polishing Sheet-Glass.—A further development of the sheet-glass manufacture in England is the process of polishing and grinding this glass by machinery. This improvement is the work of James Chance, and has produced, at a cheap price, an article equal in effect to plate-glass, and by which houses are now glazed with a glass that does not distort external objects, while, at the same time, when viewed from the outside, it has all the polish and fine appearance of plate-glass.

James Chance conceived the ingenious idea of laying every sheet of glass intended to be ground and polished upon a flat surface covered with a damp piece of soft leather. The sheet adhering completely to the leather after having been pressed against produces, in fact, a vacuum, so that by the pressure of the atmosphere the whole sheet is maintained in a flat position. Two sheets having been placed in this manner, each on the retaining or sucking surface, they are turned one against the other in a horizontal position, sand and water being constantly supplied between them; and by means of ingenious machinery, the two surfaces rapidly rub one against the other in all directions, and are ground at the same time by the sand. When the grinding has been performed on one surface, the sheets are turned and have the other surface ground in the same manner.

The sheet being ground while it is kept perfectly flat, it is not necessary to wear out more than a thin layer of the whole surface. Of course, after the operation, the sheet of its own elasticity resumes its former more or less curved shape, but this is of little consequence since the wave lines are destroyed, and both sides have a polish as perfect as plate-glass.

Melting and Fining of Plate-Glass.—Two sizes of pots are used in the manufacture of plate-glass—the larger for melting the vitreous mixture, and for keeping it long in a state of fusion—the smaller for receiving a portion of the glass to be fined and cast. The latter are termed cisterns, or in France *cuvettes*. The English pots and cisterns are of the same form as the pots used in the manufacture of crown-glass; and this is also the form of the French pot; but in France the cistern or *cuvette* is formed square or rectangular—as shown in Fig. 30—and three pots contain the material for six small cuvettes, or for three large ones. These last are employed for mirrors of large dimensions—for example, of 100 inches and upward. Latterly, furnaces have been constructed for six pots and twelve cuvettes, eight small and four large ones. The small ones have the form of a perfect square, the large ones of an oblong rectangle. About the middle of the depth of the cuvette, A A, a groove or indentation, B, is formed, whereby the vessel is grasped with the tongs.

Fig. 30.



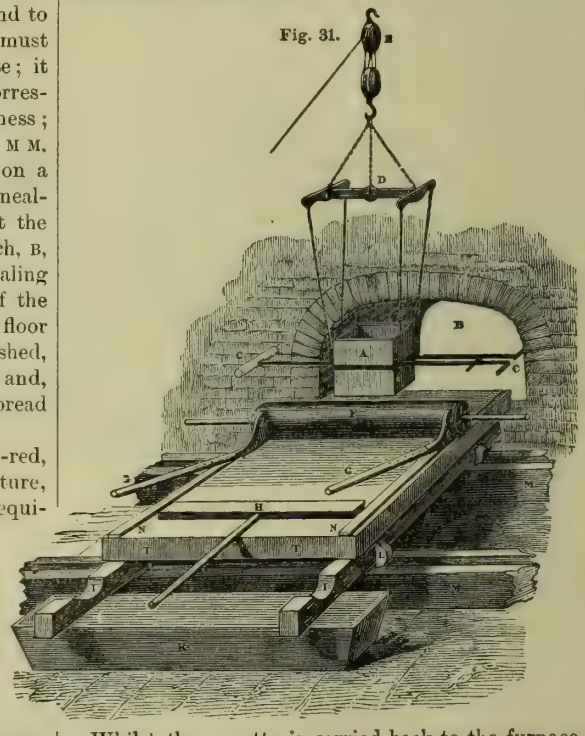
The time necessary for the fusion and the fining is in France divided equally between the pots and the cuvettes. The material is left sixteen hours in each, and at the end of these thirty-two hours it is fit to be cast. During the melting of the mixture in the pots, the cuvettes are placed empty in the furnace; but as soon as the whole charge is in a state of fusion, the cuvettes are removed by means of tongs, and cleansed from all impurity, and from the residual glass of the last operation by a scraper. They are then replaced in the furnace, and after a few moments' heating the surface of the metal in the pots is skimmed, and the liquid glass is transferred into the adjacent cuvette with a copper ladle, care being taken not to disturb any grains of sand or lumps that may have settled down at the bottom of the pot. Thus at the very commencement a kind of double purification is effected—the infusible portion is left untouched, and the glass is well mixed by the agitation of ladling. This transferring process, which is termed in France *tréjetage*, requires two workmen, one after the other; each draws out the glass three times—whence the word *tréjeter*, to throw or cast thrice—and then plunges his ladle into cold water. The furnace is then shut, and the cuvettes are left to themselves, that the bubbles excited in the mass by the *tréjetage* may be disengaged, and the excess of soda be entirely volatilized. It has been stated that the melting is generally accomplished in sixteen hours; but the fining which succeeds the ladling process must be kept up quite as long, and extends indeed sometimes to twenty-four or even forty-eight hours before the bubbles are dispersed and no more alkali is volatilized. After the p rfect

melting has taken place the glowing mass is allowed to lower its temperature a little, so as to acquire a slight degree of viscidity. With this view the fire is allowed to decline, and the glass acquires the proper consistency in three or four hours. To make sure of this the end of a rod is dipped into the cuvette; the portion taken up is allowed to hang down, and by the form it assumes and other indications the workman readily judges whether it has acquired the necessary consistence and is free from bubbles. This is termed "drawing the glass."

Casting.—While the glass is acquiring the requisite consistence, attention must be given to heat the annealing furnaces, as well as the casting-slab or metal plate which is to receive the liquid glass. This table was formerly made of bronze; but the liability of this metal to crack induced the British Plate Company to try a plate of cast-iron, which was found to be quite successful. The table, T T—Fig. 31—must be of longer dimensions than the largest plate; it varies from 10 to 20 feet in length, with corresponding breadth, and is 6 to 7 inches in thickness; it rests on a strong wooden frame or truck, M M, movable on casters, and sometimes running on a railway, along which it is wheeled from one annealing oven to another, since it is necessary that the table should be placed close to the oven or arch, B, into which the plate is to be removed for annealing after being cast. With this view the height of the slab or table is made exactly on a level with the floor of the arch. Its upper surface is flat and polished, to mould the lower surface of the mirror; and, before the casting, it is heated by hot coals spread over it, and then wiped perfectly clean.

The annealing ovens being heated to a brown-red, the casting-slab brought to a suitable temperature, and the metal or melted glass thickened to the requisite point for flowing readily and equably, the aperture into the cuvettes which are to be taken out is then opened; two workmen introduce tongs into the furnace, and grasp the cuvette by the groove shown in Fig. 30, while a third slides a large pincer under it. When this instrument is pushed well under the bottom of the cuvette, the workman draws it towards him, aided by the others with their tongs, which are supported on rollers. In this manner the cuvette is drawn to the mouth of the opening, where it is raised by a crane, placed upon a truck or low carriage, and removed to the casting-table. The melted glass being skimmed, the cuvette, A (Fig. 31), is then drawn up to a sufficient height by the tackle, D E, and suspended above the upper end of the casting-table, where it is tilted over by means of the tongs, C C, and the metal is poured out on the table. The glass is prevented from running over the sides by ribs or rims of copper, N N, which are exactly equal in height to the intended thickness of the plate of glass; and when the cuvette has been emptied of its contents, a massive hollow copper cylinder, F, 3 feet in diameter, and resting at each end on the side ribs, is set in motion. This cylinder, which weighs several cwts., is moved by means of the handles which form a prolongation of the axis, and spreads the glass out into a sheet of uniform breadth and thickness. It would, however, overflow the sides, if this were not prevented by the workmen applying the iron pieces, G G, which form a dam at the sides, and precede the course of the rollers. Lastly, to prevent any impurity from contaminating the glass, a workman draws the washer, H, covered with cloth, immediately in front of the advancing sheet of fluid glass; the excess of glass pours over the front edge of the slab into a trough, K, filled with water, and finally the roller passes off and is received in the grooves, I I. A beautiful play of brilliant colours, comprising every imaginable tint, is exhibited by the glass immediately after the roller has passed over it; caused, probably, by a temporary oxidation of the surface.

Fig. 31.



Whilst the cuvette is carried back to the furnace to receive a fresh charge of glass, the two ribs are removed, and any blisters or seams or redundancy which may exist at the two sides of the plate are broken off; a thick flange of the still soft glass is then turned up at the end, T T, and a rake-shaped iron is applied to it, by means of which the plate is thrust forward into the annealing oven, B, where it rests upon sand. As the plate is not perfectly rigid when this is done, the force which must be exerted to push it over the floor of the kiln often produces considerable undulations on the upper surface, which subsequently disappear under the polishing.

While the introduction of the plate into the annealing arch is being proceeded with, other workmen are engaged in taking from the fining furnace another cuvette, which arrives at the casting-table at the moment when the preceding plate has just been

introduced into the annealing oven. After filling the oven all the openings are carefully stopped up with iron plates and clay mixed with sand. At the end of twenty hours some of the pieces of iron are taken away; an hour or two afterwards more are removed; as the oven cools, more and more are taken away, and at last the whole of the clay and plates of iron which stopped the apertures are removed. In this country the plates are allowed to remain in the oven, resting in a horizontal position, from five to ten days.

The annealing ovens, termed in France *carquaises*, are very large and have several fire-places. The bed or floor is made of bricks, presenting in its whole extent a perfectly level surface. Sand must be sprinkled over the bed, that the plates may slide freely upon it and encounter no impediment in shrinking or contracting.

Squaring, Grinding, and Polishing.—After being withdrawn from the annealing oven, the plates have to undergo the operations of squaring, grinding, and polishing. The squaring is performed by passing a rough diamond along the surface of the glass, guided by a square rule; the diamond cuts to a certain depth into the substance, when, by gently striking the glass with a small hammer underneath the part which is cut, the piece comes away; and the roughnesses of the edge then left are removed by pincers.

The plates having been squared, next undergo the processes of grinding and polishing. In these operations two plates are employed, one of larger dimensions and one three or four times smaller, which are made to rub against each other. The lower and larger plate is embedded in plaster of Paris, in a perfectly horizontal position, upon a table about 2 feet high, which is termed the *grinding bench;* the smaller plate is cemented upon the lower face of a swing table, made heavy by weights, and caused to traverse over the lower plate in such a way that by a combination of a rotatory and oscillating motion, the relative position of the two plates is constantly changed. In adjusting the plates, a rough or rolled surface of the one is opposed to the comparatively smooth or casting-plate surface of the other, and the material employed to grind the surfaces is thrown upon the lower plate from time to time. River sand and water were formerly used for this purpose, but ground flint of different sizes is now substituted, as answering the purpose better. When one side of each plate has been sufficiently ground, it is loosened from the frame and turned over, so as to present the other surface to be ground in the same manner. Some degree of pressure is employed by loading the upper plate with weights, as the grinding of each side approaches to completion.

By means of this grinding the plates are made level, but are still too rough to receive a polish. To fit them for this, they are now ground with emery powder of increasing degrees of fineness. The lower plate is placed upon a stone bench covered with wet canvas, which holds it firmly in its place; the surface is sprinkled with emery and water, and a small plate, moved by the hand, is used as a runner or grinder. About three sizes of emery are used, the different qualities being previously separated and assorted by suspension in water; and between each size the plates, canvas, bench, and hands are thoroughly washed. After the application of the last or finest emery, the plate has become quite smooth and partly polished.

The now perfectly even plate is embedded in plaster, as already described, and polished by machinery with fine oxide of iron.

Melting and Fining of Flint-Glass.—The melting furnaces already described are equally applicable to flint-glass and other descriptions of glass, except that for bottle and crown-glass the furnaces are usually oblong, and are only constructed to contain from four to six pots; whereas for flint-glass works round furnaces, containing from eight to twelve pots, are almost exclusively used. Ten pots of 36 inches diameter are the medium number for a well-proportioned furnace, and are found the most economical for fuel. When the furnace has too large dimensions, too great an area is left unoccupied by the pots or fuel, and too small a furnace exposes the backs of the pots to hang over the fire-place in the centre, which in time enlarges by burning away, and causes the pots to crack at the bottom or back by cold draughts through the fire-bars. In some works two furnaces open into the same flue. By this arrangement, while one of the furnaces is in full operation the other may be undergoing repair.

The principal and only essential difference in the conditions for the melting and fining of flint-glass consists in the shape of the pots, which are distinguished from those employed for other descriptions of glass by being covered with a hood-shaped top, the mouth of which fits the working holes of the furnace, so that the smoke cannot contaminate the contents, as in the usual glass furnaces. Open pots are used in some parts of France for flint-glass, when dried beech or oak-wood is used for fuel, and so little carbon is produced by the smoke as not to affect materially the metal, although the flames play upon its surface; but when coal or coke is used, as in this country, the fumes and smoke emitted would carbonize or deoxidize the lead, and precipitate it to the bottom in the original metallic state, if the pots were not covered; besides that the solid particles of soot would blacken the glass, by attaching themselves firmly to its surface.

The ingredients previously mentioned, having been carefully mixed together and sifted, are brought to the furnace in wooden vessels like hand-barrows, and thrown into the pots in successive charges with an iron shovel. In this state the batch or frit, as the composition is called, is of a salmon colour, the red tinge being derived from the oxide of lead. English melting-pots, which are usually much larger than the French, hold about 18 cwts. each, and the batch is introduced in quantities of about 4 cwts. at a time, allowing a sufficient interval between each filling for melting down the various charges, until the pot is entirely filled with fused glass. By this method every pit in the furnace is fully charged with liquid metal

in about twelve to fifteen hours; air-bubbles and striæ then abound, and are not expelled until thirty to forty hours more have elapsed. During the founding the mouths are securely stoppered and clayed up, and the furnace is urged to its utmost intensity. The shorter the time of fusion and refining, the better; for this purpose the heat can scarcely be too great. With the best possible recipe, and the purest materials, good results depend upon an intense and rapid fusion: too little heat will fail to refine the metal, and drive off air-bubbles and the colouring matter of the manganese; and too long continuance of intense heat will destroy the manganese, cause the glass to attack the pot, and become striated, gelatinous, and greenish. If the glass do not get fine by the usual time allotted, but becomes coddled or gelatinous, it will never recover, however urged by subsequent fusion. Such glass must be ladled into water, and considered only as cullet for re-fusion, with a proportion of new materials. The moment the metal is fully fused, and refined by continuous rapid fusion, the high temperature of the furnace should be reduced from its maximum heat to a working temperature; this period being considered *the crisis*. When flint-glass is kept in fusion beyond the crisis, it not only assumes a greenish tint by acting upon the iron of the Stourbridge clay pot, but takes up a small portion of its alumina, which by its inferior density rises to the surface, frequently with detached portions of the pot, causing striæ and other impurities, which injure its quality for common uses and render it entirely unfit for optical purposes. Formerly, scum or sandiver was allowed to run off, or was skimmed from the surface of the pots when opened for working; but the modern relative proportions and purity of the chemical materials are so good as seldom to render this skimming necessary.

Flint-glass is either formed by simple blowing with the pipe, and then shaping by hand; or, secondly, by blowing in moulds; or, thirdly, by moulds alone, in which the glass is subjected to pressure. In each of these cases the form and appearance of the article are very generally improved by grinding, cutting, &c.

Cutting and Polishing.—The finishing process which gives to the finer articles manufactured of flint-glass their distinguishing beauty is technically termed *cutting*, but is actually performed by grinding. The operation is performed by discs of iron, sandstone, or copper, revolving in a lathe which is propelled by steam power. The edges of the discs, which are sharp, angular, or rounded, according to the work to be performed, are supplied with sand and water dropping from a hopper for *rough grinding*, and with emery for *fine grinding*. A stone-wheel with water is employed to smooth out the rough sand-marks, and prepares the glass for the *polishing*, which is effected by means of a willow-wood disc, first with a mixture of pumice and rottenstone, and finishing with a preparation of tin and lead, termed putty-powder. All table-glass ware and hollow articles are thus cut.

De la Bastie's Hardened Glass.—The inventor of this process has acted on the assumption that the fragility of glass proceeds from the weakness of the cohesion of its molecules, and that if the molecules could be forced close together, thus rendering the mass more compact, the strength of the material would be increased. In his first experiments he endeavoured to effect this by mechanical compression while the glass was in a fluid or viscid condition, but obtained only negative results. He therefore changed his mode of working, and commenced to apply to glass a system of tempering, such as is usually applied to steel—namely, submitting it to a bath of heated oil. Fused glass dropped into water becomes greatly contracted; the sudden cooling, though it hardens the outside of the glass, yet puts its whole substance in such a state of strain, and as a consequence in such a state of unstable equilibrium in its constitution, that the slightest friction of the exterior coating of hardened glass determines the destruction of the entire mass.

De la Bastie endeavoured to diminish the strain and deepen the extent of the case hardening, by tempering the glass in a fluid other than water. He states that with thick glass vessels two essential conditions must be observed:—First, that the glass must be brought to just that degree of heat where softness or malleability begins, the molecules being then capable of closing su denly together, condensing the material when it is plunged in a liquid at a considerably lower temperature; though glass when it is thin may be tempered at red heat even before becoming soft. Second, the liquid to be employed for the immersion of the glass must be such as can be heated much higher than water without boiling. For this purpose he therefore uses oils and grease, wax, resin, and tar or pitch.

In carrying out the process it is necessary that the glass to be tempered should be raised to a very high temperature; the hotter it is the less is the risk of breaking the glass, and the greater is the shrinkage or condensation. Hence the advantage and often the necessity of heating the glass to the point of softening, though attended by the difficulties that the glass gets readily out of shape, so that it must be plunged almost without touching it; and though in plunging the hot glass into a heated combustible liquid the latter is apt to take fire, and cannot easily be extinguished, so that time and material are lost. These difficulties, however, are overcome by placing the tempering bath in immediate communication with the heating oven, and covering it so as to prevent access of air. The oven being charged with the articles to be tempered, these are pushed or caused to slide into the adjoining bath without handling them, and the liquid of the bath having no supply of external air is not liable to inflame.

In order that the shape of the tempered articles may not be affected, particularly for flat glass, the floor of the oven is made to cant, so that when the glass is heated on it it is turned to a sloping position, and the glass slides into the bath along a surface therein arranged at the same slope as that of the

oven floor. Small articles may be heated on the edge of the bath, and immersed by a slight push. The clearness of the glass may be affected by the dust of the furnace flame, which is apt to settle on the glass and chill its surface. This is avoided by heating the glass in a muffle, to which the flame has no access, being applied externally. Moreover, the shock of the fall of glass into the bath is prevented by fixing therein a sheet of wire gauze or asbestos fabric, or providing a bed of sand or other like material for the glass to fall on.

Articles made of thin glass can be plunged at a lower temperature. Although the best effect is produced in all cases if the glass is plunged in the soft condition, yet with thin glass a high degree of tenacity is attained if it is plunged even while still hard.

Moreover, it is not essential that the bath should always be actually heated, so long as its temperature is below that of the glass, such temperature depending on the nature of the glass to be tempered. Thus hard glass requires to be tempered in a bath of high temperature, while glass of a soft quality can be tempered in a bath of a lower temperature; some glass can even be plunged in a cold bath at the temperature of the surrounding atmosphere. Neither is it always necessary that the substance employed should be in a liquid condition, as the necessary cooling effect may also be produced by plunging the articles into a bath composed of pulverulent material or of gaseous bodies, such as a current of air. The materials which are preferred, however, are oils or fatty matters.

Instead of effecting the tempering by one single operation of plunging, the article may be plunged several times consecutively in order to give it greater hardness, and the baths may be either of the same or of a different character; thus a bath of hot oil may be first used, and the article while still hot may be then plunged into cold or warm water; also the article may after removal from the bath be subjected to a reheating process.

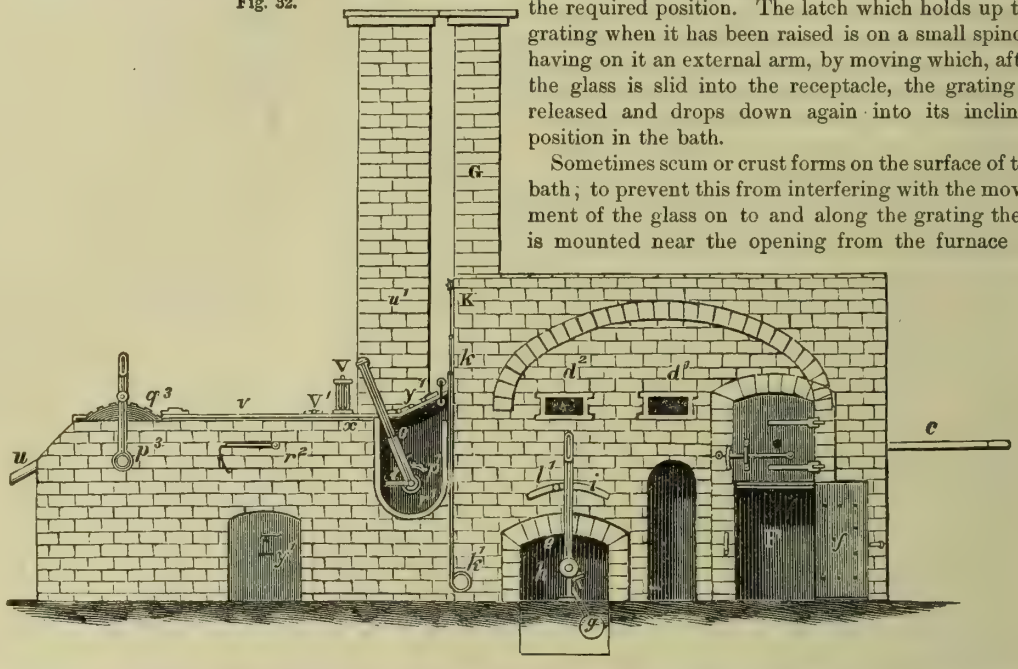
The furnaces employed for carrying out the tempering process with flat glass are constructed with a long compartment or passage at the side of the furnace, with which it communicates by means of a wide but very low opening. In this passage is an endless travelling metallic web on which are placed, one behind the other, the sheets of glass to be heated and tempered. As the sheet of glass arrives in front of the opening the workman, by means of a long flat fork passed through a side hole, lifts the sheet slightly, and pushes it through the opening into the heating chamber of the furnace, where it is received on a movable carriage consisting of a flat slab of fire-brick on a framing supported by small wheels running on rails on the furnace bed.

In order to insure the uniform heating of the sheet of glass, the carriage is moved backwards and forwards in the heating chamber by means of a long rod passed through the wall of the furnace. The bed of the furnace is constructed with a double bottom, below which is the framing and wheels of the carriage, which is thus protected more or less from the heat of the furnace, a long slot being formed in the double bottom, through which passes the support for the fire-brick slab. The slab or table of the carriage may either be fixed on its framing, or it may be made to revolve on it, in order to present all parts of the glass sheet to the action of the heat, and for this purpose it may be connected by bevel gearing to a spindle extending through the wall of the furnace. The furnace is heated by a fire-grate closed in by doors provided with eye holes; the flames pass over a bridge to the bed of the furnace, whence they pass partly through the side opening into the before-mentioned passage with travelling web, and partly to a chimney provided with a damper for regulating the heat.

When the glass sheet has been sufficiently heated the carriage is pushed towards a sole or movable part of the furnace bed, capable of being canted, on to which the sheet is drawn by means of a rake. This movable part or sole consists of a refractory slab, which may be faced with smooth porcelain supported on an iron frame, which is mounted on sliding rods that extend down to a shaft in the lower part of the furnace, where they are fitted with screws for adjusting the level of the sole. The shaft has an arm with a counterweight to balance the sole. The supporting rods between the sole and the shaft pass through slotted holes in a plate, which holes are covered by slides, so that heat cannot pass down from the furnace, nor air enter to inflame the material of the bath. The glass sheet having been drawn on to the sole, the attendant, by moving to an adjustable stop an external lever fixed on the shaft below, causes the sole to sway in an inclined attitude towards the bath, which is set in masonry adjoining the furnace. Between the furnace and the bath is a long narrow opening closed by a vertical slide, which is connected by a chain passed over pulleys to the lever that works the sole shaft, so that the slide is raised as the sole is thrust partly through the opening, without admitting flame to the bath. The glass plate slides from the inclined sole on to a grating mounted on a shaft, which passes through the bath; the grating being inclined by means of an exterior lever, so that it coincides with the plane of the inclined sole. The grating, for about a third of its length at the end next the sole, presents openings of lozenge form, and it has longitudinal bars in the rest of its length, and the lower end of the framing to which it is jointed has a cushion of wire gauze, against which the edge of the glass impinges without shock. When the glass is received on the grating the sole is moved back into the furnace, the slide closing the opening after it. When the glass has been immersed for sufficient time in the bath, the grating is by means o' the external lever raised to a horizontal position, in which it is retained by a latch; and the cover of the bath being raised, the glass is drawn by a rake into a receptacle divided by shelves into several horizontal compartments, and mounted on a shaft worked by an external lever, so that any one of these compartments can be presented on a lever with the grating for the reception of the glass sheet.

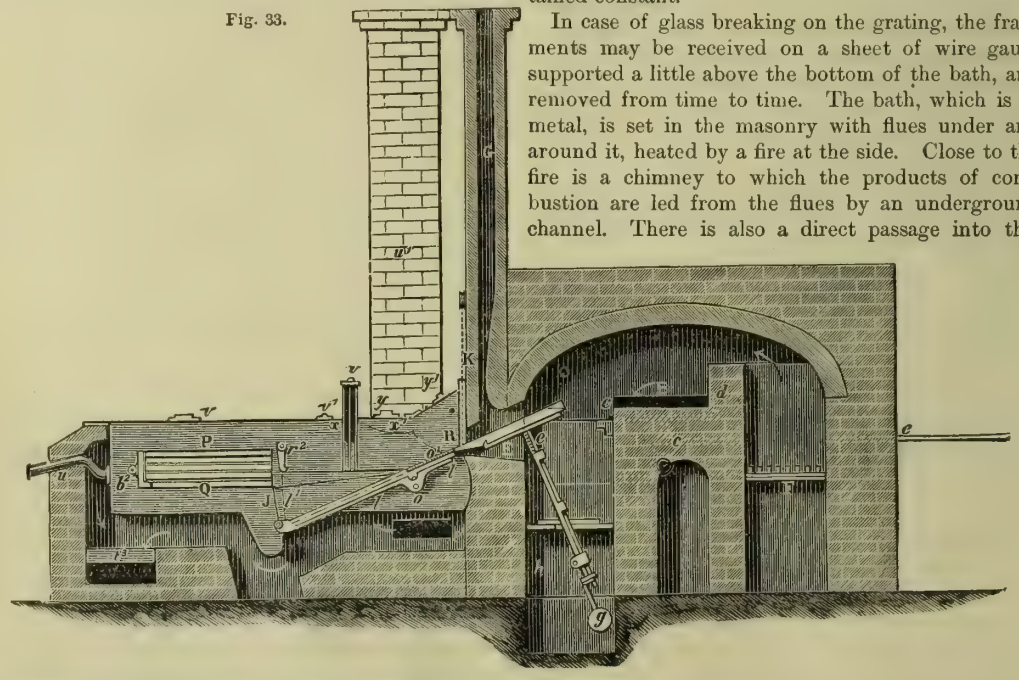
The shaft of the grating, where it passes through the side of the bath, is fitted with a conical trunnion, working in a conical seating, adjustable to prevent leakage; and the lever which works this shaft, as well as that for working the shaft of the shelved receptacle, is provided with a catch engaging with notches on a fixed sector, so as to hold the shaft in the required position. The latch which holds up the grating when it has been raised is on a small spindle having on it an external arm, by moving which, after the glass is slid into the receptacle, the grating is released and drops down again into its inclined position in the bath.

Fig. 32.



Sometimes scum or crust forms on the surface of the bath; to prevent this from interfering with the movement of the glass on to and along the grating there is mounted near the opening from the furnace an oscillating rake, worked by a spindle and external handle, whereby the attendant, before moving the sole towards the bath, removes the scum or crust into a wire gauze receptacle under the bath cover. The bath is provided with a syphon overflow pipe, in order that the level of its contents may be maintained constant.

Fig. 33.



In case of glass breaking on the grating, the fragments may be received on a sheet of wire gauze supported a little above the bottom of the bath, and removed from time to time. The bath, which is of metal, is set in the masonry with flues under and around it, heated by a fire at the side. Close to the fire is a chimney to which the products of combustion are led from the flues by an underground channel. There is also a direct passage into this chimney from the fire, and this passage, as well as that into the flues of the bath, is provided with a damper, so that according as the one or the other is more or less opened or closed the temperature of the bath can be varied.

The cover of the bath is made in several parts,

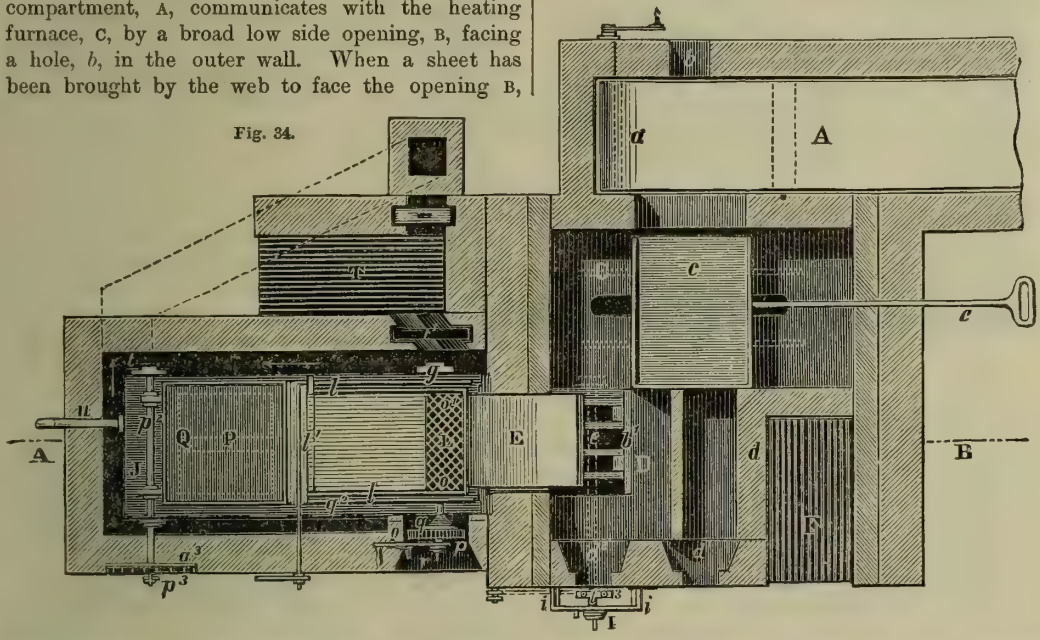
hinged so that they can be separately opened to give access to the receptacle of the tempered glass, or to the crust or scum receptacle, or to the skimming rake, and in a fixed portion of the cover is a thermometer which indicates the temperature of the bath. There may also be a pipe for leading to the chimney vapours evolved from the bath; and at the bottom of the bath there is a pipe with a stop-cock or valve for emptying the bath.

Fig. 32 represents a side view; Fig. 33, a longitudinal section; and Fig. 34, a sectional plan of the furnace and bath for tempering flat sheets of glass.

A is a side compartment of considerable length, having mounted on rollers within it a travelling metallic web, *a*, on which are placed in succession the sheets to be treated. The last of the rollers, a^1, is worked by a winch outside the wall. The compartment, A, communicates with the heating furnace, C, by a broad low side opening, B, facing a hole, *b*, in the outer wall. When a sheet has been brought by the web to face the opening B, the attendant introduces through *b* a flat fork, slightly raises the sheet, and pushes it through the hole B into the furnace, where it is heated to softening. The sheet lies upon a carriage, *c*, which consists of an iron framing, having a facing of stone or other refractory material level with the opening B, and the frame has rollers running on a pair of small rails below, and a handle by which it is moved to and fro, so as to cause the sheet to be uniformly heated. To protect the lower part of the carriage and to economise heat, a refractory arch or floor is formed a little below the table of the carriage, the stem thereof passing down through a hole which is elongated to allow of the to-and-fro movement of the carriage.

For the purpose of more uniformly heating the

Fig. 34.

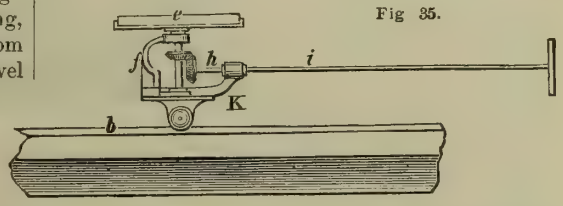


glass, the table of the carriage might be made to rotate as well as to move to and fro by constructing the carriage as shown in Fig. 35, where *e* is the refractory table mounted by a vertical spindle on the carriage, *f*, which has its rollers running on the rails, *b*. The handle, *i*, which extends through the walls of the furnace, turns in a bracket bearing, having collars on each side to prevent it from moving longitudinally, and is connected by bevel gear, *h*, to the spindle of *e*, so that by turning the handle, *i*, the table, *e*, can be rotated, and also by pulling or pushing *i* it can be moved to and fro.

In front of the compartment of the furnace, C, which contains the moving table, there is another compartment, D, which as well as C is heated from a fire, F, on the grate bars. This fire-place is provided with an ash-pit door, *f*, and a fire door, in which is a sight hole for observing the state of the fire. The flames and products of combustion passing over the bridge, *d*, heat the furnace and escape by the opening, B, heating the compartment, A. The heat within the furnace is regulated by a chimney, G, which has a damper or cap for adjusting the draught.

When the glass sheet is sufficiently heated on the table, *c*, which can be seen through the sight hole,

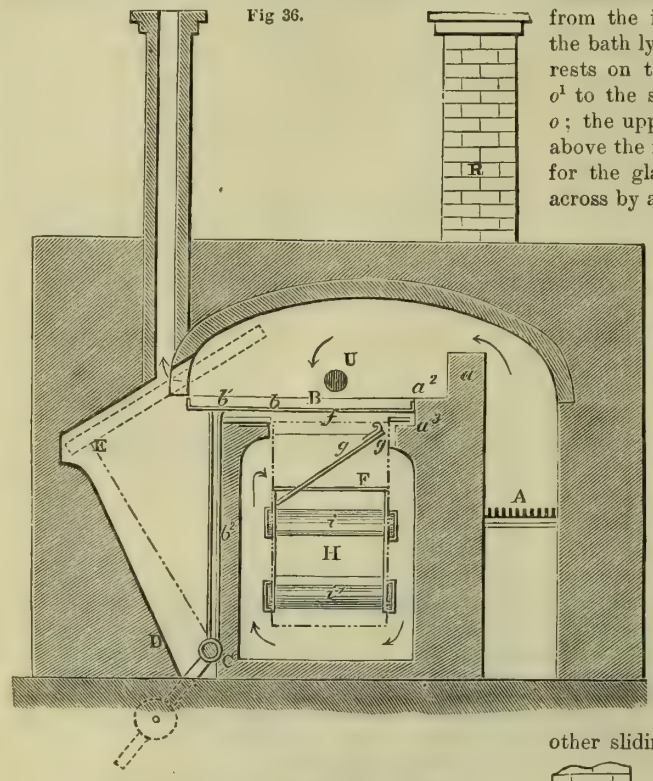
Fig 35.



d^1, the carriage is pushed close up to the oscillating sole, E, which consists of a stone or other refractory table faced if desired with smooth porcelain, and resting on a framing, *e*, carried by two arms, projecting upwards from a rocking shaft, mounted near the bottom of the furnace and carrying a counter-weight, *g*. Each of these arms is made in two parts,

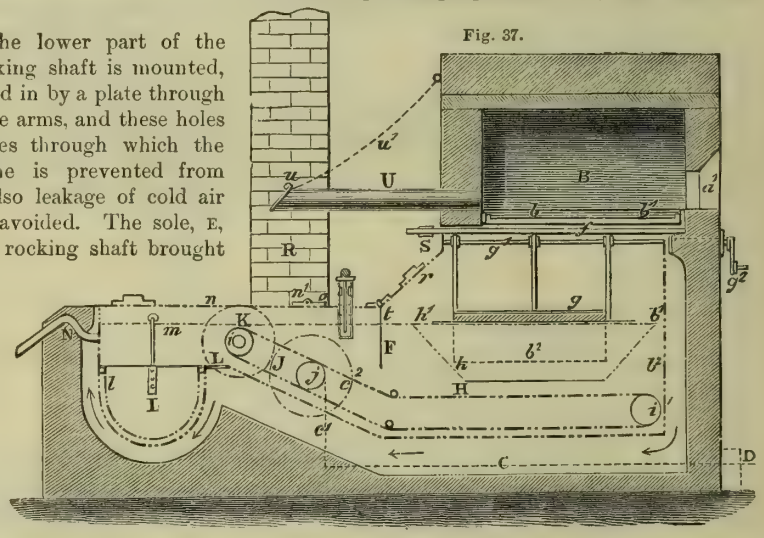
the one sliding along the other, with a screw and nut by which the height and level of the sole can be accurately adjusted. The lower part of the furnace, *h*, in which the rocking shaft is mounted, is open in front and is covered in by a plate through which are slotted holes for the arms, and these holes are covered by sliding plates through which the arms pass. Thus the flame is prevented from extending down to *h*, and also leakage of cold air from *h* into the furnace is avoided. The sole, E, being by partly turning the rocking shaft brought to a level with the table, *c*, the workman by means of a rake introduced through a side hole, d^2, draws the sheet of glass on to the sole, and then by means of an external lever, I, fixed on the shaft, *e*, cants the sole towards the mouth of the bath, J, as shown in Fig. 33. This movement of the sole is limited by an adjustable stop, *l*, on a quadrant along which the lever, I, is moved. To prevent flame from entering the bath, J, from the furnace, the mouth, E^1, is closed by a vertical slide, K, suspended by a chain which passes over guide pulleys, *k*, k^1, and is attached to the lower arm of the lever, I. When this lever is moved to cant the sole, E, into the mouth, E^1, the chain being at the same time pulled raises the slide, K, to allow for the passage of the sole. When the sole is canted back to its horizontal position where it rests against an iron bar, the chain is slacked out, and the slide, K, descends and closes the mouth of the bath. The sheet of glass sliding from the inclined sole is received on a grating in the bath lying at the same inclination. This grating rests on two side bars, l^2, l^2, which are pivoted at o^1 to the side frames, *l*, *l*, fixed on a rocking shaft, *o*; the upper edge of the side frames, *l*, rise a little above the face of the grating to serve as side guides for the glass sheet, and their lower ends are tied across by a piece of bent plate in which is placed a roll of wire gauze, l^1, as an elastic buffer to receive the glass when it slides down.

Fig. 36.



The upper part of the grating for about one-fourth of its length has lozenge or diamond openings separated by bars sharp on their upper edges, and for the rest of its length it consists of thin bars fixed at one end to the points of the diamonds, and at the other end to a cross bar joining the two side bars, l^2, l^2, and projecting a little beyond them at each side, so as to rest on the side frames, *l*, *l*. A grating of the kind described gives the liquid of the bath access to all parts of the glass. When it has been immersed for the required time the grating, L, is canted back to its level attitude by means of an external lever, O, fixed on the shaft, *o*. The lever, O, consists of two parts, the one part fixed on the shaft, and the other sliding through guides on o^2, and terminating in a claw, which resting on a toothed segment, p^1, holds the lever in any desired position. On grasping the handle at the top of the lever (which handle is made in halves, the one half fixed to o^2 and the other to o^3) the claw of o^3 is released from the teeth of the segment, and the lever can be moved. Adjustable stops, *p*, are provided to limit the throw of the lever. The shaft, *o*, is at one end pivoted in the one side of the bath, and it passes through the other side, having a cone fitting a conical seat, which

Fig. 37.



is kept tight against leakage by a spring, r, pressing against the end of the shaft. This spring also serves as a break to the movement of the shaft, and its pressure can be adjusted by a screw, r^1. A counterweight to balance the grating might be attached to the shaft o.

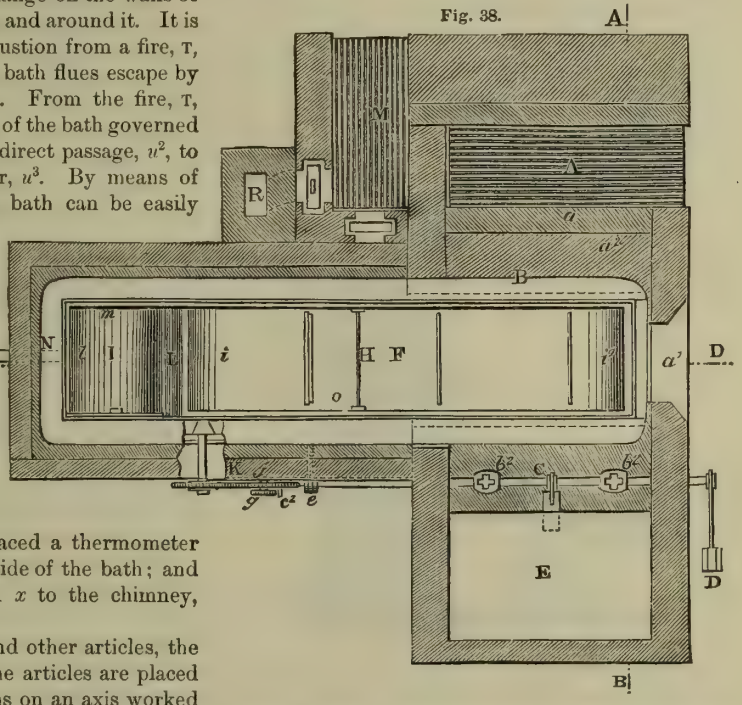
To remove scum or crust from the surface of the liquid in the bath a skimmer is placed near the mouth, E. It consists of a blade worked by an external handle, so as to push the scum along a curved plate into a small wire gauze basket, where it drains, the basket being taken out and emptied when it has been filled up. The liquid is kept down to the required level by a syphon overflow pipe, u. The bath is suspended by its upper flange on the walls of its setting, with flue space under and around it. It is heated by the products of combustion from a fire, T, which after passing through the bath flues escape by a passage, t^3, to the chimney, u^1. From the fire, T, besides the passage, t^1, to the flues of the bath governed by a damper, t^2, there is also a direct passage, u^2, to the chimney, u^1, with a damper, u^3. By means of these dampers the heat of the bath can be easily regulated.

The cover of the bath is made in several parts; the first part, v, is hinged at v^1 to a fixed part, x, so that it can be raised as a door, and there are two other doors, y and y^1, the one for access to the scum basket, and the other for observing the adjustment of the sole, E, and grating, L. In the fixed part, x, of the cover is placed a thermometer tube, V, preferably close to one side of the bath; and a pipe may be connected from x to the chimney, u^1, to carry off vapour.

For tempering glass vessels and other articles, the sole of the furnace on which the articles are placed to be heated is mounted by arms on an axis worked by an external lever. In its horizontal position this sole covers over the top of the bath, which is, moreover, closed by a sliding plate under the sole. When the articles are heated sufficiently they are moved by a rake on to a narrow lateral sole, which is fixed on a level with the movable sole. The latter is then canted to one side so as to expose the mouth of the bath, and the sliding plate being then withdrawn the heated articles are pushed into the bath. To prevent them from striking the sides there are fixed in the bath pieces of wire gauze inclining downwards towards the middle, which is open, forming a sort of funnel by which the glass articles are guided down towards the middle opening. Near the bottom of the bath an endless web of wire gauze is mounted on rollers, and guided by narrow rollers along its edges, and bars are fixed at intervals across it. The glass articles are received upon this web, and when it is moved they are carried by it upwards in a sloping direction, and finally discharged from it at one end of the bath into a receptacle made with a rounded bottom, in which receptacle there is suspended a wire gauze basket which receives them, and by means of which they are lifted out of the bath. Immediately under the sliding plate which covers the opening into the bath below the movable sole, is mounted a wire gauze rake by which the crust and scum is withdrawn from the surface of the bath before plunging the glass articles into it. This rake is worked by an external handle on its spindle, and the sole is moved by an external treadle, which is connected by ratchet gearing to one of the rollers of the endless web, so that every time the sole is moved the web is made to advance.

Fig. 36 represents a tranverse, and fig. 37 a longitudinal section; and fig. 38 is a sectional plan of this tempering oven. The wine-glasses, tumblers, and the like, having been previously heated in a separate stove, are introduced by the hole, a^1, and placed upon the sole, B, which is of stone or refractory material laid on a frame, b, supported by two arms, b^2, b^2, on a rocking shaft, C, having an arm and counterpoise, c, and an external treadle, D, by pressing down which the sole can be canted to the position indicated by the dotted lines, E, fig. 36. When the sole is horizontal it covers the bath, and is level with a shaft, a^2, at the side of the bridge, a. When the articles on the sole are properly heated they are moved by a rake on to the shelf, a^2, and then by means of the treadle, D, the sole is canted over so as to uncover the bath, whereupon the articles are pushed into the bath, and the sole is returned to its horizontal position. As the sole does not form a perfectly tight cover to the bath, a sliding plate, f, is arranged under it, the said plate being withdrawn by an external handle, f^1, at the time of plunging. A

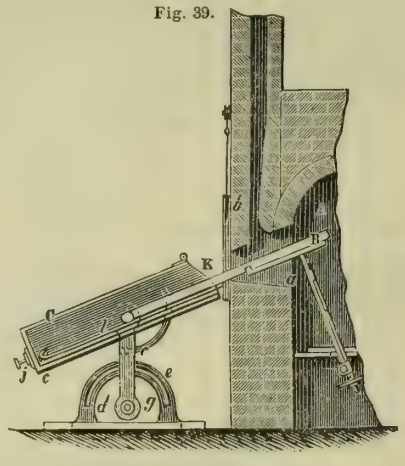
Fig. 38.



wire gauze skimmer, g, is suspended by arms from a spindle, g^1, having an external handle, g^2, and immediately before plunging the skimmer is moved so as to sweep the scum or crust to one side. The handle, g^2, might be connected to the treadle, D, so that the skimmer should be worked at the time the sole is canted over.

To prevent the glass articles from striking the sides of the bath a wire gauze basket, h, with sloping sides and open at bottom, is suspended in the bath, and its sides guide the glass on to the travelling wire gauze web, H. This web passes round rollers, i, i^1, and is guided by short rollers at its edges to follow the form of the bath bottom. It has across it bars of thin sheet metal, dividing it into lengths, one of which at each of its intermittent movements is presented under the basket, h, to receive the plunged glasses. These are carried by it upwards, and finally delivered into a wire gauze basket, l, hung by straps, m, in the well, I, of the bath. The web, H, is advanced a division every time the treadle, D, is

Fig. 39.



moved, the shaft, c, of the treadle being connected by ratchet and suitable multiplying gear to the roller, i, of the web.

The heating of the oven and bath is effected by two fires in a manner similar to that already described for sheet-glass, and the bath is provided with a cover having doors, thermometer, and other necessary fittings.

A pipe, U, having a flap door, u, may be fixed in the wall of the furnace, from which its interior will receive heat for warming small articles, such as lamp glasses, placed in the pipe before they are laid on the sole, B.

Fig. 39 represents the mouth of an oven and a portable bath which it is advantageous to use for tempering special articles, such as mirror plates or optical glasses.

The movable bath is a flat rectangular vessel containing a grating, and having one end to open. It is mounted by trunnions or arms near the mouth of the furnace, and adjusted to such an inclination as to coincide with that of the sole when it is canted. The end of the bath is opened and the sole canted towards it, causing the articles to slide from the sole into the bath, which is then closed and removed.

In front of the oven mouth is placed a jointed frame, c, provided with segments and clamping screws, so that it can be adjusted in various attitudes and angles. The portable bath, C, containing the liquid and a grating, is heated separately, and placed on the table, c, of the jointed framing, being adjusted in position by a set screw, j. For plunging, the door, K, of the bath is opened, the glass is slid on to the grating from the sole, B, the door, K, is then closed, and the bath is removed to give place for another of the same kind.

For tempering cylindrical articles, such as lamp glasses, the apparatus consists of a long spindle on which the glass is placed between two cones or between a cone and a collar. This spindle is fitted to slide through a collar, and revolves with a pinion, which can be caused by gearing to rotate with considerable velocity. The pinion and its gearing are mounted by an arm on a horizontal axis. In one position of this arm the spindle is horizontal, or nearly so, and can be slid with the glass on it through an opening into the furnace, where, being caused to revolve, the glass becomes uniformly heated. The arm is then moved into an inclined attitude, when the end of the spindle with the glass on it is canted down into a bath below the furnace chamber.

Fig. 40 represents part of the section of a bath with apparatus for tempering lamp glasses or tubes generally; Fig. 41 is a front view of the apparatus. A frame, a, is pivoted at b, and has a strong pin, d, bearing on an arc, c, giving friction sufficient to support the frame in any attitude. On the frame, a, is mounted a drum, K, which can be turned by a winch handle, m, and there is also mounted in two bearings, f, f, supported from the frame, a, by a column, e, a sleeve, i, on which is a small pulley bearing against the drum, K, and driven from it by frictional contact. Through the sleeve, i, slides a rod, n, which may be square in section or fitted with a feather, so that it must turn with i, but can slide freely through it. On the one end of the rod, n, is swivelled a ball handle by which the rod can be pulled or pushed while it revolves; at the other end is a cone, on which is placed the lamp glass. The workman pushes in the rod, n, so that the glass enters a hole in the furnace or a heated pipe like U (Fig. 37), and turning the drum, K, causes the glass to revolve rapidly, so as to become uniformly heated to the required temperature; he then draws it back till it is over the bath, as shown in Fig. 40, and raising the frame, a, causes the apparatus to take the inclined position indicated by the dotted lines, the glass being plunged into the bath.

Fig. 42 and Fig. 43 show rods, i, such as n above referred to, for holding glasses, either cylindrical, pear shaped, globular, or of other round forms, collars, a and b, of porcelain or other refractory material being fitted on them when required to hold the glasses in place.

Tongs of various forms may also be employed to hold between their jaws the glasses to be tempered

while they are being heated, so that on opening the jaws they drop into the bath, and when such tongs are employed they are made with a third arm besides the two which work the jaws, this arm having attached to it a ring, or parts of a ring, by moving which the glass is separated from the jaws when it happens to adhere thereto.

Fig. 44 is a side view, and Fig. 45 a plan of tongs

Fig. 40.

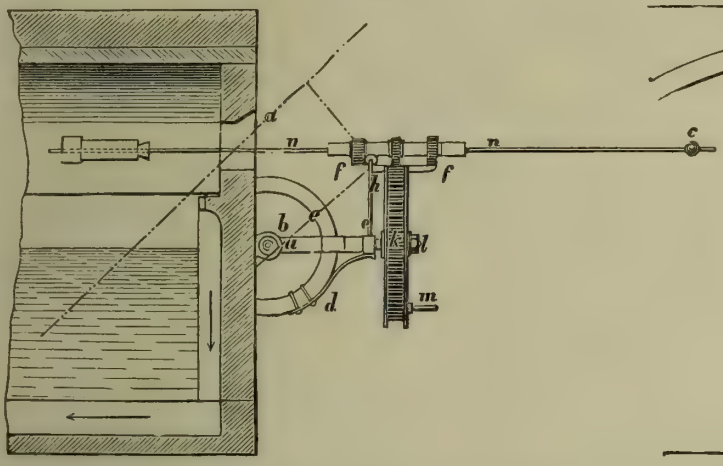
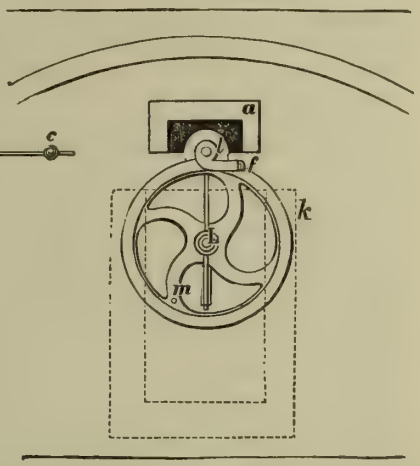


Fig. 41.



for lamp glasses. *a* are the jaws of the tongs worked by the handles, *a'*, *a'*; and *b* is a ring embracing the glass, and worked by an intermediate handle, *c*, so that should the glass tend to adhere to either of the jaws when they are opened, it can be detached by moving the ring, *b*.

Fig. 46 shows a rod, *i*, with a hollow cylinder, *c*, of pipe-clay or other refractory material held between claws, *b*, projecting from a boss, *a*. A glass tube or other cylindrical article is placed in the inside of the cylinder, *c*, which can be rotated, and when heated is dropped out into the bath by canting the cylinder downwards.

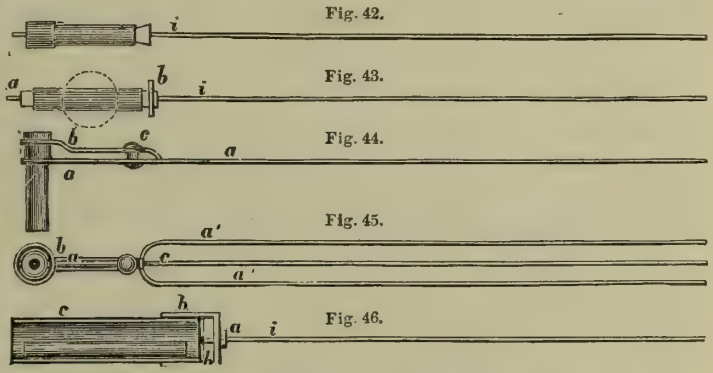
Small articles, such as dishes, cups, and the like, may be heated in refractory moulds, so as to avoid spoiling their shapes, and plunged by inverting these moulds and allowing them to drop into the bath.

The applications of the tempered or hardened glass are limited by its peculiar properties. It cannot be cut with a diamond, and if the outer cuticle is fairly cut through the whole mass disintegrates. In spite of this disadvantage it has nevertheless already come largely into use, and when the process is further developed, and the whole of the conditions for successful working are known, it may lead to the adoption of glass for many purposes for which it is at present unsuited.

H. J. Powell of the Whitefriars glass works writes:—After a rough trial of this process, which certainly answers well for flat or solid glass, we decided that it is defective for hollow flint-glass, since hollow vessels, if left to themselves in a kiln, are almost certain to collapse on reaching the required heat. To avoid this difficulty, and knowing that a vessel in course of manufacture, however hot, is always under control whilst it remains on the workman's rod, we placed a bath as near the mouth of the working pot as possible, and directed the workman, instead of sending the finished vessel to the annealing oven, to drop it into the bath.

The vessel is caught in a wire net, and is ready for removal as soon as it has acquired the temperature of the bath.

For all vessels made in one piece, *e.g.*, tumblers,



finger glasses, &c., this process answers well, and it is obvious that if it proves to be the best way of treating hollow flint-glass, the use for this description of glass of the complicated machinery described above will be done away with, and the glass will be tempered in the course of manufacture, instead of being reheated and tempered after it has been already manufactured and annealed.

We ascertained, with M. de la Bastie's aid, the right constituents and right temperatures of a bath for flint-glass; for although the conditions for sheet, and plate, and flint glass are nearly the same, there

is a difference, and it seems probable that every chemically different glass, and even every different thickness of glass, may require certain variations.

In our experiments on the hardness of the glass, we found that it could be marked, but not cut with the diamond; and although it could be smoothed and engraved in the ordinary way, that the disturbance caused by the wheel, when penetrating to any appreciable depth, tended to weaken, or even to cause the destruction of the entire mass.

The value of the invention, as far as it concerns flint-glass, is therefore at present somewhat modified by difficulties in manipulation.

It seems to be impossible to heat a vessel made up of different pieces, and of various thicknesses, to an absolutely equal temperature throughout, so that the whole may be equally tempered.

It seems also impossible to displace the air from a narrow-mouthed vessel sufficiently quick for the inside and the outside to be tempered simultaneously.

Moreover, setting aside these difficulties, we come to a point which applies equally to all kinds of hardened glass. Hardened glass is not "unbreakable;" it is only harder than ordinary glass, and though it undoubtedly stands rough usage better, it has the disadvantage of being utterly disintegrated as soon as it receives the slightest fracture, and up to the present time of being undistinguishable from ordinary glass.

A piece of hardened glass is only a modified Rupert's drop, *i.e.*, it is case-hardened; the fracture of both is identical, both resist the diamond, and both can be annealed. Moreover, in the middle of imperfectly hardened glass, a line is plainly visible, which marks the extent of the case-hardening. This line resolves itself under the microscope into a mass of bubbles and striæ; it seems to be the nucleus of breakage, and consequently as soon as the cutting-wheel approaches it, the glass falls to pieces.

Coloured Glass.—The revival of the taste for stained glass windows and the manufacture of coloured flint-glass, first in Bohemia, and afterwards in all parts of Germany, in France, and in England, has directed the attention of glass manufacturers to the colouring of glass by metallic oxides, and has caused the re-discovery of a lost art.

When glass painting is the object, the colouring matter is applied either as a pigment or in a melted state on the glass. When the colour is to be given throughout the entire substance, a peculiar glass, termed, from the name of its inventor, "Strass," is sometimes manufactured as the basis, more particularly when imitations of precious stones are desired.

For this purpose a glass is required possessing the highest degree of transparency, combined with the greatest possible lustre. These requirements are found in a composition analogous to that of flint-glass, but containing a much larger proportion of oxide of lead and a little boracic acid. Donault-Wieland recommended, by way of example, either of the three following mixtures:—

	No. 1.	No. 2.	No. 3.
Ground rock-crystal,	100	—	100
Sand,	—	100	—
Pure minium,	156	—	154
White-lead,	—	171	—
Purified caustic potash,	54	3?	56
Boracic acid,	7	9	6
Arsenious acid,	·3	·3	·16

Strass, when well prepared, possesses as nearly as possible the high refractive power and all the other properties of the diamond, except its hardness.

The choice of the crucibles is very important, since they sometimes colour the metal yellow or brown, when particles of iron are detached from the internal surface. This inconvenience is not to be apprehended with crucibles of hard porcelain, but these often break or run out, and are too permeable. Hessian crucibles are the best. A pottery or porcelain furnace is used to melt the material, and the crucibles remain in the fire about twenty-four hours. The more tranquil and prolonged the fusion, the greater hardness and beauty does the strass acquire.

Yellow is produced either by charcoal, antimony, silver, or oxide of uranium. The charcoal, incorporated with the glass in a very fine state of division, produces a dirty yellow, which, as the quantity increases, passes into a dark brown without lustre; it is, therefore, little used as a pigment. A much superior yellow is obtained by roasting sulphide of antimony to the state of antimonious acid, and melting it with 3 to 5 per cent. of undecomposed sulphide of antimony. An *orange yellow* is prepared with glass of antimony, minium, and a little oxide of iron. In these cases the substances so prepared are mixed with the materials of the glass. When silver is employed the process is quite different; in this case a mixture of powdered clay and chloride of silver is applied to the surface of the ready-made articles, and on reheating these in a muffle, the silver penetrates to a certain depth into the glass even before the latter softens; the article is then allowed to cool, and the coating which was applied is scraped off, when a yellow colour of great brilliancy appears on the glass. It is remarkable that this effect can only be produced on glass containing alumina. Oxide of uranium produces a beautifully delicate yellow of a slightly greenish hue; but this pigment is too costly for common use.

Red, of different shades, is communicated by oxide of iron, suboxide of copper, or different preparations of gold, mixed with other materials. The oxide of iron is employed either as pure ferric oxide, prepared by heating the nitrate, or in the state of bloodstone or ochre. This substance added to the glass mixture produces a cheap and very common brownish red.

The application of gold to produce a brilliant red colour, which, according to circumstances, can be made to assume a scarlet, carmine, rose, or ruby tint, was first introduced by Kunckel, who used for the purpose the brownish-red precipitate produced in a solution of chloride of gold by a salt of the sesquioxide of tin. Fuss has shown that ruby-coloured glass may be obtained when the powdered ingredients for the glass are mixed, previous to

fusion, with oxide of tin and the solution of gold; the mixture then appears like moist grey sand. The simple addition of a solution of gold to the flux, without any oxide of tin, is likewise capable of producing rose and carmine-coloured glass.

Blue is produced by oxide of cobalt. The colouring power of the oxide of cobalt is so intense, that pure white glass is rendered sensibly blue by the addition of $\frac{1}{1000}$th part of the oxide.

Green may be produced either by protoxide of iron, protoxide of copper, or oxide of chromium. The tint produced by the first of these substances has little brilliancy. The oxide of copper yields a beautiful emerald. For this purpose the glass is mixed with the product obtained by heating copper to redness with access of air, or with powdered verdigris, which is then decomposed in the fire, and converted into oxide by oxidizing agents. Care must be taken to prevent the protoxide of iron from being converted into sesquioxide, and the oxide of copper from being reduced to suboxide. The oxide of chromium, which occurs as a pigment in commerce, yields the purest and most brilliant grass-green hue.

The following are the approved recipes for imitating precious stones:—

Diamond.—Colourless strass, without any addition.

Topaz—

Very white strass,	1000
Clear yellowish orange-red glass of antimony,	40
Purple of Cassius,	1

A very good imitation of topaz is obtained from—

Strass,	1000
Oxide of iron,	10

Ruby.—The preparation of topaz furnishes a means of obtaining constantly and at pleasure very fine rubies. The mixture for topaz often gives an opaque mass translucid at the edges, and presenting in its thin plates a colour red by transparency: 1 part of this opaque topaz-matter, and 8 parts of strass melted in a Hessian crucible, when left thirty hours in the fire of a potter's furnace, give a fine yellowish crystal similar to strass. Remelted with the blowpipe, this produces rubies of the finest water.

A ruby not so fine, and of a different tint, may be made by employing the following proportions:—

Colourless strass,	1000
Oxide of manganese,	25

Emerald.—The emerald is very easy to imitate. That which succeeds best results from the mixture of the oxide of copper with colourless strass. If oxide of cobalt be added, the green obtained presents blue reflections. The composition which gives the best imitation of natural emerald is as follows:—

Colourless strass,	1000
Pure oxide of copper,	8
Oxide of chromium,	0·2

By increasing the proportion of chromium or oxide of copper, and adding oxide of iron to the mixture, one may vary the green shade, and imitate peridot or dark emerald.

Sapphire.—To produce a fine oriental blue colour, employ very white strass, and very pure oxide of cobalt. This composition, put into a luted Hessian crucible, should remain thirty hours in the fire. The proportions are:—

Colourless strass,	1000
Oxide of cobalt,	15

Amethyst—

Colourless strass,	1000
Oxide of manganese,	8
Oxide of cobalt	5
Purple of Cassius,	0·2

Syrian Garnet.—The artificial garnet is a kind of dark ruby, and is made after the following formula:—

Colourless strass,	1000
Glass of antimony,	500
Purple of Cassius,	4
Oxide of manganese,	4

In the fabrication of artificial stones, the materials must be pulverized with great care. The mixtures can only be well made by repeated sifting. The same sieve must not be used for sifting different compositions, whatever care be taken to clean it after each operation. Lastly, to obtain masses well melted, quite homogeneous, without striæ or bubbles, it is necessary to employ substances very pure, and mixed in a state of extreme division; to obtain the best crucibles, to melt with a graduated heat, in a furnace which is quite equal in its maximum temperature; to leave the metal in the furnace during twenty-four to thirty hours, and to cool the crucibles very slowly, that their contents may undergo a kind of annealing.

Coloured Flint-Glass.—Assuming as the composition of the glass to be coloured the common ingredients and proportions, and remembering that these materials, when mixed together, are technically termed "batch," and when used with the usual precautions produce a highly pellucid flint-glass, this may be regarded as the basis of the following coloured glasses.

Soft White Enamel.—To 6 cwts. of batch add 24 lbs. of arsenic, 6 lbs. of antimony.

Hard White Enamel.—To 6 cwts. of batch add 200 lbs. of putty prepared from tin and lead.

Blue Transparent Glass.—6 cwts. of batch coloured with 2 lbs. of oxide of cobalt.

Azure Blue.—6 cwts. of batch with about 6 lbs. of oxide of copper.

Ruby Red.—6 cwts. of batch with about 4 ozs. of oxide of gold.

Amethyst or Purple.—6 cwts. of batch with about 20 lbs. of oxide of manganese.

Common Orange.—To 6 cwts. of batch add 12 lbs. of iron ore and 4 lbs. of manganese.

Emerald Green.—To 6 cwts. of batch add 12 lbs. of copper scales and 12 lbs. of iron ore.

Gold Topaz Colour.—6 cwts. of batch with 3 lbs. of oxide of uranium.

Bontemps points out that the colouring properties of metallic oxides are greatly modified by the degree of heat to which the glass is subjected, and by other circumstances.

Iron.—It is generally agreed that oxide of iron gives a greenish colour to glass, to the mixture of

which it has been added; but the truth is that this colour is produced only in peculiar circumstances. The manufacturers of china, porcelain, and earthenware are well aware that oxide of iron is the colouring material of a fine purplish-red enamel; if the temperature is raised too high, this enamel tends towards orange.

If into a pot containing white melted flint-glass a small piece of iron is introduced during the blowing, it will from its gravity fall to the bottom, and the whole of the glass in its neighbourhood will be coloured from orange to yellow. But when glass is melted at a high temperature, as, for example, in making window-glass, the addition of a small quantity of ferric oxide produces a bluish colour. It is also known by the manufacturers of bottle-glass, that when cooled in the pot it becomes opaque blue before being devitrified.

Thus glass may receive all the colours of the spectrum from oxide of iron; and, moreover, it may be observed that these colours are produced in their natural order as the temperature is increased.

Manganese gives to glass a purple or pink colour; but if the glass remains too long in the melting furnace, this colour becomes brownish-red, then yellow, and afterwards green.

Copper, in its highest state of oxidation, gives to glass quite free from iron a sky-blue colour, and in its lowest state of oxidation a ruby colour.

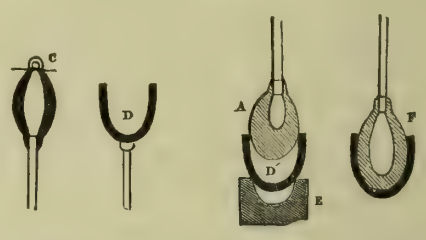
At all times, as at the present day, red window-glass has always been coloured by protoxide of copper; but it is not very easy to obtain this colour, because it is not at all fixed: it must be seized at the proper time.

When the glass is in the proper state to be blown, if it is ladled into water, yellow-green cullet is produced; if this cullet is heated to the point of liquefaction and cooled slowly, the red colour will gradually show itself as the glass cools, becoming of the finest ruby, inclining more to orange than to purple. In some cases the cooling in the usual process of manufacture does not produce this colour, and it is necessary to expose the glass to the temperature of the annealing kiln, in which case the red colour is seen to increase gradually till it arrives at its greatest intensity. If this ruby glass is over-fired it changes, first to crimson-red, then to purple, by a greater degree it takes a bluish tinge, and afterwards gets discoloured.

Flashing and Casing.—This process consists in coating a layer of colourless with one of coloured glass, which can then be reduced by grinding to the proper tint. For this purpose the glass blower collects the proper quantity of colourless glass on the end of his pipe, rolls it upon the marver, and then dips it for a moment into a pot of melted coloured glass, and blows out the two together into a cylinder or globe, which is flatted or *flashed* out in the usual way. In this manner panes for the glass-painter are formed, which consist of two layers of glass, one coloured, the other colourless; and the former can be ground down to any required tint or degree of transparency.

Flint-crystal glass is usually coloured by a somewhat similar process termed *casing*. Presuming that any two or more glasses intended for casing have been mixed of the same specific gravity, to give them the capability of harmonizing—that is, of contracting and expanding equally—the blower has to gather a ball of solid glass, intended for the inner layer, in the usual manner (Fig. 47). About the same time

Fig. 47.



his assistant prepares a casing of coloured glass, D, knocking off the knob to open and shape it somewhat like the bowl of a wine-glass, or the broad end of a large egg-shell; this is set into a metal stand, E, on the floor, merely to steady the case or shell, D; while the blower takes the lump of flint or white glass, A, and gently blows it into the coloured case or shell, D′, to which it immediately adheres; and when submitted to the flame of a pot-hole, it is found to weld perfectly, as F.

Glass-Painting.—Painting on glass is performed by means of a vitreous mixture termed the flux, combined with a pigment prepared from some metallic oxide. The flux and oxide are simply that combination of ingredients which is necessary to produce a highly fusible coloured glass of the required hue; this mixture is reduced to a state of fine powder, rubbed up in oil of turpentine, boiled oil, or sometimes simply with water, and laid upon the glass to be painted by means of a brush. The glass thus painted or stained with the intended design is then exposed to a heat sufficient to vitrify the mixture without melting the glass; in other words, the painting is said to be burnt in; the ingredients of which it is composed are converted into a coloured glass or transparent picture, while the pane or other article on which it is laid is only sufficiently softened to cause the complete adherence of the coloured glass to its surface.

It is evident, therefore, that the fusing point of the pigment must be much lower than that of the glass to be painted. Indeed, it is necessary that the former should vitrify at a temperature at which the latter does not sensibly soften; for any considerable softening or yielding of the glass would distort the design. Hence the manifest inapplicability of crystal or lead-glass for painted articles, on account of its great fusibility. On the other hand, common window-glass, or even plate-glass, may be successfully used, and, best of all, the hard Bohemian glass, which contains potash for a base.

When the colouring oxides employed are such that they are not injuriously affected by the oxides of lead

and of bismuth, the flux is usually composed of the following ingredients:—

	Parts
Quartz in powder,	100
Oxide of lead,	125
Oxide of bismuth,	50

But if these oxides exert an injurious action on the colouring matter, and tend to change its shade, the subjoined composition is used:—

	Parts.
Quartz in powder,	100
Fused borax,	75
Nitrate of potash,	12·5
Carbonate of lime, free from iron,	12·5

To either of these mixtures or fluxes the proper colouring matter is added, and the composition so formed is introduced into a crucible, and melted into a coloured glass. The latter is then reduced to a fine powder, mixed, as has been stated, with oil of turpentine, and used as a common pigment for painting on the less fusible glass. In this operation a cartoon, or drawing upon paper, is placed below the glass, and the colours are applied on the corresponding lines. In preparing painted sheets or panes of glass, brown or black outlines are generally traced on the one side of the sheet, whilst the colours are laid on the other side; but in painting vessels or other articles, this is not the practice.

One great difficulty of the glass-painter consists in this, that the colours which he lays on have not the same appearance as they are intended to assume in the finished work. When the same figure or pattern is to be repeated many times, it is, in some cases, printed on the glass with a gentle pressure from an engraved metallic plate, or wooden block, boiled oil being used as the vehicle for the colouring oxide. The pane, having been prepared either by painting or printing, is exposed in an oven or muffle to a temperature sufficient to fuse the vitreous flux and dissolve the colouring material.

Professor BARFF describes the method pursued in the manufacture of stained glass windows as follows:—After a design has been drawn, in which the effect of the window as a whole can be carefully considered, cartoons of the figures and ornaments are made of the exact size of the intended painting, the lines being extremely clean, precise, and well drawn, because it is from these that the workman, who is not usually himself an artist, has to convey on the glass the feeling of the artist.

The cartoon when completed is laid down in pieces for convenience sake on a table, and fastened with small nails. The glass-cutter then selects the various coloured glasses which are required to be inserted in their proper places, so as to carry out the design. For instance, a piece of white or yellow tinted glass is cut to the shape of the face. If the figure be a small one the hair also is included in this; and probably in the figure of a saint the nimbus which surrounds the head may be included; while in larger figures the face is of glass of one tint, the hair of another, and the nimbus of one or more tints, different from these.

The outlines of the figure are painted with a substance called "tracing brown," made by mixing some oxide of iron with a flux, heating them together in a crucible, and grinding the product to a fine powder, which is mixed with the articles adapted to the particular use to which it is to be applied.

Different fluxes are employed by different glass painters: some contain borax, because these fluxes fuse more easily. These are, however, liable to become hydrated, and in this condition often cause the painting to peel away. Harder fluxes are the best, though they require more heat. Lead fluxes are sufficiently fusible for all ordinary purposes, and are not liable to the objection of those containing borax.

Suppose it is desired to paint the outlines of a face, the glass is cut to the shape denoted in the cartoon; it is then laid upon the cartoon, and the painter seeing the lines through the glass, traces them with his brown paint. He generally uses gum water as his vehicle, and puts on the shading also with the gum mixture, though sometimes it is found necessary to use a substance which is not affected by moisture, as, for instance, tar oil. When the face is finished it is removed, and another portion of the figure proceeded with; and so on till by a repetition of this process the figure is completed, when all the parts are put on the cartoon, in order to see that the whole is harmoniously treated.

In shading, a glass easel is used, on which the figure is put together, and the parts made to adhere by wax, so that the artist is able while painting to form an idea by transmitted light of the effect which will be produced when the picture is finished.

When all the glass is painted it is fired in a muffle, upon the proper construction of which a great deal depends. It is usually made of iron, and should not be more than 15 inches from its bottom to the top. It is never well to have it longer than about 2 feet wide by 2 feet 6 inches deep. The top of the muffle is usually slightly arched from side to side, and it is placed in the furnace on a tolerably thick stone floor, so that the bottom may not get too hot. The fire, which is lighted below, is allowed to play up its sides and over its top, the flue being so placed as to draw the flames in that direction. The muffle has ridges in its sides to receive iron plates, and there is generally about an inch, or rather less, between the top of one plate and the bottom of another. The plates are covered over with perfectly dry powdered chalk or whiting, and the pieces of glass are laid upon them with their painted sides uppermost. The muffle has two doors, between which is a conical tube to enable the workman to look in from time to time to see that the glass is not overheated. When the firing is completed, the muffle is allowed to cool slowly, in order to anneal the glass.

When the pieces of glass are perfectly cold they are united by peculiarly shaped strips of lead. The lead has a thick core, and at right angles to the bottom and top of this are thin plates called the leaves. The core is drilled with little ridges so as to enable the workmen to bend the lead about with facility. The joints of the lead are soldered, and

the interstices between it and the glass filled up with a cement made of white lead, oil, and plaster of Paris—in fact, a fine kind of putty.

Soluble Glass.—See Soap and Sodium Silicate.

GLUE. — *Gelatin*, *Bone Gelatin*, *Animal Glutin*. *Gelatine*, *Colle forte*, French; *Gallerte*, *Leim*, *Tischerleim*, German (see Bone).—The term gelatin is applied to that part of animal matter of which the aqueous solution, fluid whilst hot, becomes a jelly on cooling.

This was for a long time regarded as a peculiar organic principle, and was known by the name of *gelatin*; but latterly Muller found it to consist of gelatin, properly so called, and of another particular product, which he denominated *chondrin*. It is generally assumed, though not perhaps on very sufficient grounds, as Brande remarks, that the gelatinous textures do not contain ready-formed gelatin; that that substance does not, in fact, pre-exist in the animal kingdom, but that it is generated by the action of hot water upon the membranous tissues.

The historical information connected with this substance is very limited. *Ichthyocolla*—the Latin synonym for *isinglass*, derived from two Greek words, signifying *the glue of fish*—is repeatedly mentioned by Dioscorides and Pliny; the latter writer attributes the discovery of it to Dædalus.

Properties.—When *pure*, gelatin is almost colourless, transparent, hard, and endued with great but variable coherence, according to the kind of tissue from which it is obtained. It is inodorous and insipid, is not affected by the atmosphere, and is neutral to litmus and turmeric. Its specific gravity is greater than that of water. When heated, it softens, diffuses a peculiar odour, enters into a state of semi-fusion, bends, tumefies, and then exhales the odour of burnt horn. In the air it takes fire with difficulty, smokes, flames only some instants, and leaves a bulky charcoal difficult to incinerate, the ashes of which consist principally of phosphate of lime. By dry distillation, gelatin gives much carbonate of ammonia, and yields the ordinary products of the distillation of nitrogenized substances.

In cold water it softens, intumesces, becomes opaque, but does not dissolve, and increases by about 40 per cent. in weight. It, however, dissolves in hot water, and the concentrated solution is precipitated by alcohol. A liquid which contains $\frac{1}{100}$th part of its weight of gelatin becomes viscous on cooling; but when it has only the $\frac{1}{150}$th, the menstruum remains fluid. If the solution of the gelatin is effected too quickly, the jelly obtained is less firm. Moreover, the result varies, not only in gelatin obtained from different tissues, but also with that obtained from the same tissue taken from animals of various ages.

It differs also according to the care which has been taken in the preparation of the gelatin; when its solution has been exposed to a temperature higher than 212° Fahr., and when it begins to sour, it loses in part the property of becoming jellied. The same happens when its solution is heated and cooled several times. If gelatin be left a long time in the open air, at a temperature of 60° to 68° Fahr., it becomes ammoniacal, and putrefies. The addition of a certain quantity of acetic acid prevents the putrefaction without destroying its adhesive power.

Gelatin is not sensibly soluble in ether or alcohol, and when the latter is poured into a luke-warm and somewhat concentrated solution of gelatin, the latter coagulates in a white, coherent, elastic, and slightly fibrous mass, which adheres to the vessel with much force. Like dry gelatin, it softens in cold water without dissolving in it. On evaporating the alcohol there remains a thin transparent coating, very soluble in cold water, but which is not capable of being jellied. Common gelatin, in a dry state, treated with alcohol, gives up to it a certain quantity of fatty matter, and some substances of an extractive nature. It is per fectly insoluble in ether and in oils, both fat and volatile.

Gelatin, when in the jellied state, and treated with alcohol, undergoes a dehydration, under the influence of which it contracts much. It was by this means that Gonnor succeeded in remarkably reducing the size of a print obtained in a very hydrated film of gelatin, and transferring it, so reduced, to stone, from which he obtained a new impression, quite similar to the first, but more or less diminished.

By taking these prints, on the contrary, with gelatin very little hydrated, and afterwards steeping them in water, a dilatation of the plate is obtained, which enlarges the figures with the same regularity.

When a solution of gelatin is continuously boiled, it by degrees loses the property of gelatinizing on cooling; this property, however, is recovered on precipitating the gelatin with alcohol.

Concentrated sulphuric acid poured on aqueous gelatin produces a very remarkable alteration in it, converting it into glycocine (sugar of gelatin), leucine, &c.

Nitric acid, aided by heat, transforms gelatin into oxalic acid.

Concentrated acetic acid renders softened gelatin transparent, and then dissolves it; the solution does not become viscid, but preserves its adhesive property. Diluted acids, on the other hand, do not prevent gelatin from coagulating on cooling.

The alkalies when dilute, and even concentrated ammonia, do not deprive it of the property of becoming jellied, but render the solution turbid by causing a precipitate of phosphate of lime. Softened gelatin dissolves at the ordinary temperature in concentrated aqua potassæ, leaving a white residuum, which is composed principally of phosphate of lime. If the solution be exactly saturated with acetic acid, and evaporated, it does not become glutinous; the gelatin, altered and combined with acetate of potash, which remains after the evaporation, is soluble in alcohol. Sulphuric acid precipitates from this liquid sulphate of potash, combined with modified gelatin; and if the precipitate be dissolved in water, and the liquor left to spontaneous evaporation, it crystallizes to the last drop. The aqueous solution of the salt is abundantly precipitated by the infusion

of nut-gall, by chloride of mercury, and by the sesquisulphate of iron. Hydrate of lime does not alter the solution of gelatin, which dissolves much of it. The same may be said of phosphate of lime; hence the reason why so large a quantity of this salt occurs in the glue of commerce.

Silver and gold salts do not precipitate gelatin, but by the influence of solar light a portion of the metal is reduced. It is thrown down by sulphate of platinum in brown viscous flakes, which blacken on the filter, and are afterwards easily pulverized. E. DAVY regards this salt as an infallible test for the detection of gelatin, even in the presence of albumen, and in solutions so dilute as to be unaffected by tannic acid.

Gallo-tannic and other tannic acids form compounds with gelatin. When added to a solution containing only $\frac{1}{5000}$th part of gelatin, nebulosity is immediately apparent. When more concentrated gelatinous solutions are treated with tincture or infusion of galls, a dense white subsidence occurs, which on desiccation becomes brownish-yellow, agglutinates, and forms a hard, brittle mass, easily reduced to powder.

From the investigations of MULDER, it appears that several definite and permanent combinations of gelatin with tannic acid are capable of being formed. On commingling the pure solutions of these bodies, a neutral combination, containing one equivalent of gelatin, one of tannic acid, and two of water, is formed. According to DAVY, the compound of gelatin with oak-tannin consists of—

	Centesimally.
Gelatin,	54
Tannic acid,	46
	100

SCHIÉBEL, who obtained nearly the same results, says that 100 parts of gelatin precipitated with a large excess of a solution of extract of oak-bark in 9 parts of water, combined with 118·5 parts of tannic acid. When, on the contrary, he mixed a very dilute solution of extract of oak-bark with the solution of gelatin, without precipitating the whole of the latter, the deposit, which occupied a considerable time in subsiding, contained 59·25 per cent. of tannic acid. The gelatin was combined in each of these cases with different proportions of tannin, which were to each other as 1·0, 1·5, and 2·0.

It would sometimes be important in researches relative to animal chemistry to be able to separate tannin from gelatin, but this has not been effected. A dilute solution, either of caustic alkali or carbonate, extracts much of the tannic acid, and leaves a gelatiniform, mucilaginous, swollen mass, which with the aid of heat dissolves in alkali like gelatin, but it is found in this case that the solvent employed for removing the tannic acid has also taken up a certain quantity of gelatin; and if the mass in question be digested with water, a little of the gelatin dissolves out, while the remainder is converted into that combination of gelatin and tannin which has been already mentioned as so slow in depositing.

Ultimate analyses of gelatin have been made by numerous chemists, but with different and ill-agreeing results, the foremost among them being those of MULDER, SCHERER, and GOUDŒVER: the formulæ proposed to represent its composition are consequently equally diverse.

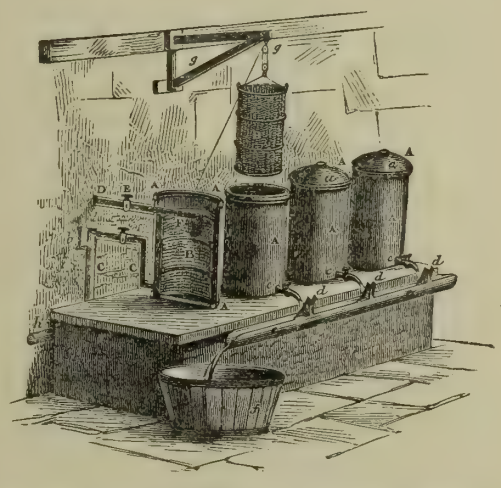
	Centesimally represented.			
	Mulder.	Scherer.	Scherer.	Goudœver.
Carbon,	50·04	50·4	50·78	50·00
Hydrogen,	6·47	6·9	7·15	6·72
Oxygen,	25·13	23·8	23·75	
Nitrogen,	18·36	18·9	18·32	
	100·00	100·00	100·00	

PREPARATION.—Gelatin is obtained by subjecting fragments of hoofs, horns, hides, bones, the feet of calves, cows, sheep, &c., to the action of boiling water or steam. The resulting liquor is skimmed and strained, so as to effect the removal of floating fatty bodies, and of any deposit which might be formed; then allowed to gelatinize by spontaneous decrease of its temperature.

It may also be procured from shavings of hartshorn, the product being tasteless, and having the advantage of being entirely free from fatty and oleaginous matters.

When gelatin is used as an article of food, the material should be of the best description, and quite fresh. Bones intended for this purpose ought to be well preserved in brine, or to be dried in a stove. Their gelatin is best extracted by the combined action of steam and a current of water percolating the fragments. Cast-iron cylinders are generally used in this part of the process. A vertical section of one of these is represented in Fig. 1, where A A A

Fig. 1.



show the exterior cylinders, containing a basket or cage, B, filled with bruised bones; C C the pipe conveying steam to the interior; D, a pipe for the introduction of water, provided with a stopcock, E, for regulating the quantity of the supply, and to which is accurately fitted a tube of tinplate, F, closed at the inside end, and perforated on its under side with small holes, so as to allow of the percolation of the

water. this tube is inserted in its proper place after the bone-cage has been introduced.

The cylinders, represented by A A A A, are elevated about 20 inches from the floor, and secured in their respective positions by screws; *a a* are the lids, in which are tubulures or valves; a thermometer is placed at *b*; the stopcocks, for withdrawing the gelatinous liquor, are shown at *c c*, *d d* are small gutters of tinplate; *e e*, the main conduit of discharge into the cistern, *f*; *g g*, blocks and tackle for raising the bone-basket; *h*, the main steam-pipe.

When a pure jelly is required, the cylinder, after being charged with bones, is wrapped in a strong, coarse woollen material; as soon as the fatty matters cease to flow, the stopcock, E, which admits the cold water, is closed, as also those at the bottom of the cylinders, *c c c*, which are to be opened only at the end of every hour, but to such an extent only as to let the gelatinous solution run out, without allowing any steam to escape. The liquid is subsequently strained, and poured into shallow vessels of tinplate, or upon slabs of marble, slate, or compact and polished stone, to solidify. It is finally cut into shreds, &c., as may be thought proper.

In GEORGE NELSON'S process cuttings are made of the hides of beasts or of the skins of calves. The cuttings being well washed are macerated in caustic alkali at a temperature of 60° Fahr., until they are partially softened. Ten days is the period named as required to effect this. They are then placed in close vessels, and permitted to remain until a thorough softening—ascertained by passing a fork through them—is effected. They are now washed in a revolving cylinder, through which a current of water passes; exposed in a well-closed chamber to the action of sulphurous acid; submitted to pressure to remove the adhering water; and subjected to the action of steam at about 150° Fahr., till they are as far as possible dissolved. The liquor is then strained, and set aside at a temperature of 100° to 120° Fahr., for the impurities which may have remained to subside; then poured upon slabs of slate or marble to the depth of about half an inch, and allowed to remain there till it has sufficiently solidified, when it is cut, and washed to remove all traces of acid. It is subsequently redissolved by means of a steam-bath at a temperature of 85°, and finally re-solidified, and desiccated by exposure to dry air upon nets.

C. R. ROPER prepares gelatin from bones or ivory, broken into small pieces in a digester. To each cwt. of material is added 6 gallons of water, and the vessel being closed, steam is admitted at a pressure gradually raised to 32 lbs. per square inch for three and a half hours, when the charge is withdrawn. The product is then run into shallow tins or pans to solidify, and finally placed on nets to dry in the usual manner.

Chondrin.—This substance resembles gelatin so strongly that it was long confounded with it. It is prepared by boiling cartilages of the ribs, &c, which have not been subject to ossification, with water, and evaporating the liquid to a jelly.

Chondrin differs from gelatin in that it is precipitated from solution by nearly all acids. The precipitate formed by hydrochloric, sulphuric, nitric, phosphoric, phosphorous chloric, or iodic acid, redissolves in excess of the acid, whilst that formed by addition of pyrophosphoric, hydrofluoric, carbonic, arsenic, acetic, tartaric, oxalic, citric, or sulphurous acid, remains permanent.

Chondrin is more particularly distinguished from gelatin by its nonprecipitation by mercuric chloride, and by its precipitation by sulphide of aluminium, alum, the acetates of lead, sulphates of iron, nitrates of mercury, and ferric chloride.

Glue is an impure desiccated gelatin, obtained from various sources. The principal substances employed are scraps of ox and other thick hides, which afford the strongest product; the debris of the tan-yards, of leather-dressers, morocco-leather manufacturers, &c. The tendons and intestines of many animals, rabbit skins deprived of their fur, scraps of parchment, old gloves, and many other apparently worse than useless matters, all contribute their quota in the manufacture of glue.

When the fresh glue-yielding substances are not to be immediately employed, it is always requisite to submit them to some antiseptic treatment till they are required for use.

These results are obtained by simply macerating them during fifteen to twenty days in milk of lime, which is repeatedly renewed. After taking them from the lime bath, they are spread in the open air to drain and dry. The desiccation is accelerated by turning them over with a fork several times a day. When sufficiently dried, the materials are packed up and sent to the glue factory.

The lime water dissolves the blood and attacks the epidermis, and predisposes the tissue to be converted into gelatin.

Formerly the glue pieces, having been cleansed as above described, were thrown loose into the caldron, which was of copper, rather shallow in proportion to its area, and flat-bottomed. Above the true bottom there was a false one of copper or iron, perforated with numerous holes, and standing upon feet 3 or 4 inches high, the animal matters being thus upheld from contact with the fire.

Now, however, the material is placed in a wide-mouthed bag or net, made of rope, and spread open in the cauldron, which contains a light framing of iron to prevent the bag adhering to the sides or bottom. Water is then added and gradually brought to ebullition. As the animal substances decrease in bulk fresh additions are made, the whole being occasionally agitated or pressed down by means of poles.

The progress of the operation is readily ascertained by withdrawing a sample of the liquor and setting it aside for a few minutes to cool. If a clear and firm jelly be obtained, the boiling has been carried to a sufficient extent, and the mouth of the glue-bag having been securely tied up, it is slowly raised by appropriate machinery until it comes in contact with, or is partially coiled round, a large beam immediately above the caldron, which

expels the fluid. In this state it is left to drain. The solution in the boiler will require evaporation before it is sufficiently concentrated for making glue.

The contents of the bag are subjected to ebullition for a second and a third time, and by this means afford *size*. When the resulting solutions are too dilute for either glue or size, they are employed instead of water for extracting the glue from fresh materials; the refuse in the bags, after all available matter has been extracted, is sold for manure, and thus every particle of animal substance is turned to account.

When sufficiently concentrated the glue is transferred from the caldron to the *settling-back*, where such a temperature is maintained that its fluidity is preserved. The impurities by this means subside, and should the manufacturer wish a very fine product, he at this time adds such fining or clarifying agents as he may prefer.

The glue is run off hence into wooden *coolers* or *boxes* about 6 feet in length, 2 in depth, and 1 in breadth. The apartment in which this is done ought to be as cool and as dry as possible, and the floor should be kept scrupulously clean, so that should any glue escape it may be recovered.

Having become a firm jelly, the glue is cut out into cubic masses, each of which is deposited in a kind of wooden box, open to the back in several slits or divisions, of a size corresponding to the thickness which the cakes of glue are required to have. It is then cut into slices by passing a brass wire stretched in a frame like that of a bow-saw along the slits. The resulting cakes of glue are deposited upon nets, which are stretched in wooden frames, and are thus removed to the sheds, where they are placed in piles, due intervals being allowed for the circulation of the air. They are turned two or three times a day.

The drying of the glue is the most precarious part of the manufacture. The least disturbance of the weather may injure the product during the first two or three days of its exposure. Should the temperature rise considerably, the gelatin may become soft and unshapely, so much so as to run through the meshes upon the pieces below, or to get attached to the strings and surround them so as not to be separable without plunging the net into boiling water. If frost supervene, numerous cracks may be formed in the cakes from the congelation of their water. Such pieces must be remelted. Even a slight fog produces upon newly-exposed glue a serious deterioration; the damp condensed upon its surface occasioning a general mouldiness. A thunderstorm sometimes destroys the coagulating power in the whole laminæ at once, or causes the glue to *turn* on the nets. A wind too dry or too hot may cause it to exsiccate so quickly as to prevent it from contracting to its proper size without numerous cracks and fissures. Thus the manufacture can only be profitably and conveniently carried on in temperate and equable weather. The drying, however, is not entirely finished in the open air. When the glue is about three parts dry it is removed into lofts, where in the course of some time the hardening is completed. But as the surfaces of the cakes become mouldy and soiled, it is necessary to scour them with a brush and hot water and set them up to drain. They are then finally dried in a stove-room at an elevated temperature, which, when they have once become solid, only serves to harden and improve them.

In France a considerable quantity of glue is made from bones, which are digested in hydrochloric acid, for the purpose of removing the phosphate of lime.

The following is the *modus operandi*:—It is proper to observe that all bones do not answer for this manufacture. Only spongy bones can be used; the ribs, the back-bone, the lower jaw-bone of animals, and the horns, are those which yield the greatest amount of gelatin. The bones are broken as small as possible by means of an axe. Some hydrochloric acid of 36° Twaddell is mixed with a quantity of water, so as to reduce the mixture to 13°, which can be ascertained by means of the acidimeter. The crushed bones are put into a vessel, and the above-mentioned preparation poured over them so as to cover them completely. The vessel is covered close with a wooden lid, and the bones are thus left to macerate for thirty hours. When this period has elapsed, it must be seen if the bones are softened; for otherwise, if the acid was deficient in strength to extract from them the lime and alkali, in that case it would be requisite to change the vessel and to give them a new maceration with a mixture of 9° Twaddell strength. When sufficiently prepared they are withdrawn and thrown into a bath of weak lime-water, where they are left to steep eight days; they are then removed, washed with fresh water, and put to steep in a fresh portion of water daily for ten or twelve days, for the purpose of removing from the bones the acid which may have penetrated them —then dried. This glue possesses little cohesive force. It dissolves almost entirely in cold water, which is the best criterion of its imperfection.

Glue is commercially judged of by its colour, and freedom from cloudy or black spots when held up before the light.

Fresh glue dries much more readily than glue that has been once or twice melted. Dry glue absorbs different quantities of water in proportion to its quality, and on this property SCHATTENMANN has proposed a method of testing it.

Dry glue is immersed for twenty-four hours in water at a temperature of about 60° Fahr. A jelly is thus formed, the qualities of which will fairly represent those of the glue. For example, the finest ordinary glue, or that made from white bones, absorbs in the time specified twelve times its weight of water, so that a plate weighing 3 grams produces 39 of fine elastic jelly. Glue from dark bones takes up nine times its weight of water, and a soft brown jelly is produced, devoid of elasticity and consistency, and falling to pieces when handled.

Well-dried glues are much less hydrometric than badly made ones, or those fabricated from inferior materials. The latter are liable to putrefaction.

Isinglass.—Colle de poisson, French; *Fischleim*, German; *Ichthyocolla*, Latin. The repeated mention by Dioscorides and Pliny of *ichthyocolla* has already been noticed.

Isinglass is obtained from the air-bag, or sound, as it is sometimes termed, of various fishes, the species of many of which are still unknown. The finest kinds are produced by species of the *Acipenser*, and some other genera, as the *Morrhua*, *Silurus*, and *Gadus*.

The method of preparing the air-bags for sale differs considerably, according to the country in which it is conducted. The commercial *pipe*, *purse*, and *lump* isinglass consist of the bag desiccated, but unopened. The *leaf* and *honeycomb* kinds are examples of the bladder cut open and dried unfolded; in the *staple* and *book* varieties it is folded, while in the *ribbon* isinglass it is rolled out. It is *picked* or *cut* before importation into Great Britain.

The isinglass produced in the Russian empire is principally obtained from the sturgeons. These cartilaginous fishes constitute the genus *Acipenser*. But this is not the only genus from which isinglass is obtained in Russia, for it is also procured from the *Silurus glanis*, which Royle suggests may be the source of the Samovey isinglass of commerce.

Russian isinglass is thus prepared:—The swimming bladder is cut open, washed, and then exposed to the air with the inner silvery membrane turned upwards. The latter is then stripped off and placed in damp cloths, or left in the outer covering, and kneaded. It is then taken out of the cloths, and either merely dried (*leaf* isinglass) or twisted in a serpentine manner, between three pegs, into the shape of a horse shoe, heart, or lyre (*long* and *short staple*), or folded in the manner bookbinders fold printed sheets of paper (*book* isinglass).

According to T. W. C. Martin, the swimming bladders are first placed in hot water, carefully deprived of adhering blood, cut open longitudinally, and exposed to the air, with the inner delicate silvery membrane upwards. When dried, this fine membrane is removed by beating and rubbing, and the swimming bladder is then made into different forms.

Several kinds of leaf isinglass are imported from Russia. The finest kind is that from Astrakhan, one variety of which is said to be obtained from the Beluga (*Acipenser huso*). These are imported from St. Petersburg. The Samovey leaf is an inferior kind brought from Taganrog. Sisane leaf is the produce of a small fish, each piece measuring only about 2½ inches each way, and weighing about a drachm; it looks like pieces of dried bladder, marked by two fibrous or muscular bands. Kroski isinglass is in small circular membranous discs. Long staple isinglass is of fine quality, and is the produce of the Oural. It is usually imported loose; at times it is strung on ropes, and this latter kind is preferred. Of short staple, three varieties are known; the finest is from the Oural, and is distinguished by the name of Patriarch, but it is very scarce. The Astrakhan short staple is one of the best kinds. The Samovey short staple is of inferior quality. Two sorts of book isinglass are met with; that from the Oural is excellent, but the Samovey product is little regarded. Siberian purse isinglass is of moderately good quality, and is in general demand. A small kind on strings, in a necklace form, is sometimes imported.

Brazilian isinglass is imported from Para and Maranham, and, according to Guibourt, is sometimes denominated Cayenne isinglass. The fishes which produce it are not known; but it is obvious, from a superficial examination of the commercial specimens, that they must have been obtained from at least several species or genera. Yarrel suggests the genera Pimelodus and Silurus as the sources of it.

It comes over in the form of *pipe*, *lump*, and *honeycomb*.

Pipe Brazilian isinglass must have been procured from a large fish. It is prepared by drying the swimming bladder unopened, and in some cases this is found distended with air. Each air-bag or *pipe*, as it is called, is from 10 to 12 inches in length, and 2 or 2½ inches broad, weighing about 5 ozs.; in shape somewhat conical, tapering at one extremity, but broader at the other, where on each side is a cæcal prolongation. It is devoid of smell. Lump Brazilian isinglass consists of two swimming bladders placed side by side, considerably separated at one end, but communicating with each other at the diverse extremity. When perfect, each specimen bears some resemblance to that of a torpedo. A perfect, though not very large lump, measures 8 inches in length, and at the greatest latitude, 5 inches. Its weight is about 6½ ozs. It consists of three portions, separated by constrictions. The largest portion is 5 inches broad, and 3½ inches in length, flattish in front, rounded posteriorly. It consists of two sacs, placed one on each side. The middle portion is oblong, 3 inches in length, and 2 in breadth. This is also formed of two sacs, communicating with the preceding portion. The third portion is oblong, 1½ inch long, and three-fourths of an inch wide. This consists of one sac only, into which both sacs of the middle portion open.

Honeycomb Brazilian isinglass appears to be the largest quantity of the lump variety split open. The latter is sometimes softened, and rolled out into thin ribbons, in this country. On account of its deeper colour and less solubility, Brazilian isinglass is not in demand for domestic use; though, as it is sold in the cut state, it is probably largely intermixed by shopkeepers with the finer kinds of Russian isinglass, and sold as such. As it is moderately cheap and soluble, it is in extensive use for fining by brewers, who are the principal consumers of this variety. When digested with boiling water, it leaves a large proportion of undissolved white matter of a starchy consistence.

Occasionally, ribbon isinglass is imported from New York. It is in thin strips of several feet long, and from 1½ inch to 2 inches in width. It is less soluble than Russian isinglass, and affords a dark-coloured solution. J. V. C. Smith states that it is obtained from the air-bladder of the common Hake —*Gadus merluccius*—which is macerated in water for a short time, and is then taken out and subjected to

pressure between two iron rollers, by which it is elongated to the extent of half a yard or more. It is then carefully dried, packed, and sent to market. The common cod—*Morrhua vulgaris*—yields a poorer kind of isinglass; but the hake only is known to the extensive manufacturers as fit for their purposes.

Hudson's Bay Isinglass.—This isinglass comes over in the purse form It is of a light yellow colour, translucent, and free from taste and smell. The inner lining of the sac, which may be readily stripped off, is insoluble in water; the remaining membrane dissolves in boiling water.

For a long period isinglass has been exported from Calcutta to China. It is probably the produce of a species of *Polynemus*.

Picked East India isinglass is in small shreds, 2 or 3 inches long, and tapering at the extremities. It is hand-picked in India by the natives.

Manilla isinglass has been imported recently as *thin cake*. It is white and clean, and is equal in quality to Brazilian or Samovey book. The fish which yields it is found in the river of Manilla, and on the coasts of the Philippines, Luconia. It is smaller than the Brazilian, but greatly resembles the lump variety of that kind, and the fish is probably an allied species.

Cod sounds, in a dried state, are brought from Scotland, and used as a substitute for foreign isinglass. They are, however, usually preserved soft by salting, and dressed for the table.

The properties of isinglass are nearly the same as those of gelatin.

The more common kinds of isinglass, especially the coarse Brazilian, are used by brewers for fining beer. They are also employed for the clarification of wines and various other liquids.

Court plaster is formed by brushing a solution of isinglass, mingled with a little tincture of benzoin, over black sarsenet.

Marine glue, *diamond cement*, *&c.*, are made by dissolving isinglass in dilute alcohol.

GLYCERIN.—*Propenyl alcohol; glycérine*, *glycérin*, French; *glycerin*, *oelsüss*, *oelzucker*, German; *elaiosaccharum*, Latin($C_3H_8O_3$ or $C_3H_5(OH)_3$).—SCHEELE, its discoverer, termed it the sweet principle of fat. This body is produced from most fixed oils and fats by the process of saponification. It does not exist ready formed in the fats, but is formed from them, together with a fatty acid, by addition of the elements of water, just as alcohol is produced from acetate of ethyl.

Most fats and oils are mixtures of propenyl ethers of the fatty acids and the acids of the oleic series. When fats are heated with water or with alkaline solutions, they are converted into glycerin and fatty acids or their alkali salts, namely, soaps.

Glycerin was discovered by SCHEELE in 1779. He obtained it in the course of making lead plaster. Olive oil, or any of the natural fats, was boiled with litharge and water till saponification was effected; the fluid remaining was then decanted, and sulphuretted hydrogen passed through it till the whole of the lead was precipitated as sulphide. After filtration the liquid was evaporated with great care below 212° Fahr., when a viscous fluid remained: this was glycerin.

Pure glycerin is a colourless, transparent liquid, inodorous, and of a syrupy consistence, possessing a very sweet taste. Its specific gravity is 1·27, at 15·°5 C. When exposed to strong winter cold it has been found to solidify to a crystalline mass resembling sugar-candy, and composed of shining octahedral crystals about the size of peas, having a strong refracting power, grating between the teeth, and exhibiting the reactions of pure glycerin. In small quantities these crystals melted quickly; but after complete fusion the glycerin did not again solidify, even when cooled far below the freezing point of water (GLADSTONE, CROOKES). According to WERNER, cold commercial glycerin crystallizes when chlorine gas is passed into it. Glycerin solidifies at —40° C. to an amorphous mass. When distilled alone it is decomposed for the most part; but when under slight pressure, or in an atmosphere of steam, it distils without decomposition.

Glycerin is soluble in water (which it absorbs from the air), alcohol, and chloroform, but is insoluble in ether. Thrown upon live coals, or heated in contact with the air, it burns with a blue flame. The alkalies, and so many metallic salts, are dissolved by it that it ranks next to water as a solvent.

KLEVER states that 100 parts of glycerin dissolve at 15·°5 C.:—

	Parts by Weight.		Parts by Weight.
Alums,	40	Phosphorus,	0·20
Ammonium carbonate,	20	Potassium arsenate,	50
Ammonium chloride,	20	Potassium bromide,	25
Arsenious acid,	20	Potassium chlorate,	3·50
Arsenic oxide,	20	Potassium cyanide,	32
Atropine,	3	Potassium iodide,	40
Atropine sulphate,	33	Quinine,	0·50
Barium chloride,	10	Quinine tartrate,	0·25
Benzoic acid,	10	Sodium arsenate,	50
Boric acid,	10	Sodium biborate,	60
Brucine,	2·20	Sodium bicarbonate,	8
Calcium sulphide,	5	Sodium carbonate,	98
Chinchonine sulphate,	6·70	Sodium chlorate,	20
Cinchonine,	0·50	Sulphur,	0·10
Cupric acetate,	10	Strychnine,	0·25
Cupric sulphate,	30	Strychnine nitrate,	4
Iodine,	1·9	Strychnine sulphate,	22·50
Lead acetate,	20	Tannic acid,	50
Mercuric chloride,	7·50	Tartar emetic,	5·50
Mercuric cyanide,	27	Urea,	50
Morphine,	0·45	Veratrine,	1
Morphine acetate,	20	Zinc chloride,	50
Morphine hydrochloride,	20	Zinc iodide,	40
Oxalic acid,	15	Zinc sulphate,	35

Glycerin can be obtained from the mother liquor of soap factories by adding to it a slight excess of sulphuric acid, heating the solution with carbonate of barium, filtering, and after the filtrate has been concentrated by evaporation, extracting the glycerin with alcohol. On distilling off the spirit, the glycerin remains. It may likewise be readily prepared by dissolving castor oil in absolute alcohol and passing hydrochloric acid gas through the fluid. The fatty ethers are washed away by water, and the residuary fluid affords the glycerin in a state of purity on evaporation. Any adhering fatty matter is separated by digesting the liquid in ether and decanting the latter.

The separation of the glycerin is, however, much more economically effected by Reynold's process. He first reduces the liquid by evaporation, and then subjects it to the action of jets of superheated steam at the temperature of 380° to 400° Fahr., which raises it to the boiling point and evaporates the glycerin, carrying the vapour upwards with it and leaving the salts to deposit in the vessel. Any tinge of colour is removed by filtration through animal charcoal or by chlorine gas.

Cap's process for the preparation of glycerin from the mother waters of the saponification of stearin with lime in the manufacture of stearic acid candles, is as follows:—The liquid drawn off from the lime-soap is reduced by evaporation in steam kettles over a naked fire; and after ascertaining how much lime is present, the necessary quantity of sulphuric acid to precipitate the lime is added.

After its subsidence, the clear liquid is decanted into another receptacle, in which it is boiled out of contact with the air, and stirred at the same time by some mechanical arrangement. This ebullition expels all the volatile fatty impurities which may be present, and, consequently, the liquid loses both colour and odour. As soon as the solution arrives at a density of 14° Twaddell, it is allowed to cool, when the precipitation of a further portion of sulphate of lime occurs. Should an excess of acid be present, some chalk or powdered limestone must be added fractionally till the liquid is neutral. After this the boiling is continued as before out of contact with air, during which time the contents of the vessel must be actively stirred, till the solution marks 37·5° Twaddell. The sulphate and carbonate of lime are now collected on a filter, and the filtrate reduced by evaporation till, upon cooling, it marks 49°, care being taken to keep it well agitated during the time. If any further quantity of sulphate of lime falls, a repetition of the filtration is necessary. To remove the tinge, the fluid is passed through washed animal charcoal or bone black, when a pure colourless solution of glycerin is obtained, marking 45°; and by carefully concentrating it further, a fourth of its weight of water may be removed, when the residuary sirupy fluid indicates 51·2° Twaddell.

A much more economical method, and one which insures the absence of all mineral impurities, was invented by Tilghmann in 1854. By his process the fatty bodies are broken up into acid and basic substances, through the agency of heat, pressure, and steam, and form separate layers in the receiver, into which the products flow from the condenser. The glycerin, which is the heavier of the two, forms the lower stratum, and the fatty acids the upper; the latter can be readily separated mechanically, and the former left devoid of any other impurity excepting water. By careful concentration, the aqueous matter may be expelled, and the product obtained of a specific gravity of 1·24, and containing only 4 per cent. of moisture; but by prolonging the operation 2 per cent. more of water may be removed, and pure glycerin is left of a density = 1·260. This process, as subsequently developed by Wilson and Payne and others, is the one by which the greater part of the glycerin in commerce is produced.

Wilson, by injecting superheated steam into a hot solution of fat, succeeded in effecting the decomposition of the latter; the stearic acid and glycerin being carried over into the receiver, where they form two layers, as in the preceding instance, and can be readily separated. See Candle and Soap.

Glyceric Acid.—Glycerin is oxidized by nitric acid into glyceric acid ($C_3H_6O_4$) and racemic acid, and by the further oxidation of this latter formic, glycollic, and oxalic acids are likewise produced.

To prepare glyceric acid glycerine is mixed with an equal volume of water, and poured on the top of strong nitric acid in a tall glass jar; or the nitric acid may be introduced below the liquid by means of a long-necked funnel (100 parts glycerin, 100 water, and 100 to 150 fuming nitric acid, are good proportions — Watts). The two layers of liquid gradually mix, assuming at the same time a blue colour, and the oxidation of the glycerin proceeds, accompanied by a copious evolution of gas. If the liquid becomes too hot the jar must be stood in cold water. The oxidation is completed in five or six days, when the strongly acid liquor is divided into small portions, and evaporated at 212° Fahr. to a syrup. The united residues are then diluted with water and neutralized with chalk, the calcium salts being subsequently precipitated by strong alcohol. The liquid is carefully separated from the precipitate; the latter is treated with warm water; and the filtered solution treated with sufficient milk of lime to render it alkaline: a calcium salt of another acid is precipitated, the excess of lime is then removed by passing carbonic acid, and the liquid is then evaporated till crystallization sets in, when glycerate of calcium is formed. Glyceric acid is obtained by decomposing the calcium salt with just enough oxalic acid to precipitate the lime, and evaporating the filtrate on a water bath (Debus).

Another mode is to evaporate the product of the nitric oxidation on a water bath, dissolve the sirupy residue in water, and then neutralize with lead oxide or carbonate. The lead glycerate is purified by recrystallization, and an aqueous solution of the pure salt decomposed by sulphuretted hydrogen. On evaporating the filtrate on a water bath, glyceric acid remains as a thick, sirupy, very sour liquid (Beilstein).

Glyceric acid is isomeric with pyruvic acid: when fused with caustic potash it is resolved into acetic acid and formic acid.

Glyceric acid after being heated for some time is converted into a soft, very tenacious brown mass, having the composition $C_3H_4O_3$, glyceric anhydride, which at a higher temperature gives off acid vapours and burns with flame (Debus).

The glycerates are for the most part crystalline soluble compounds. Only one atom of hydrogen is replaced by the metal, though glyceric acid is triatomic; its salts therefore have the composition, $C_3H_5MO_4$.

Glycerin, Nitro-. See Explosives and Nitro-Glycerin.

GOLD.—French, *Or;* German, *Gold;* Latin, *Aurum.* Symbol, Au.

Specific gravity varies from 19·258 to 20·72, according to the state in which it exists. Equivalent, 196·67, BERZELIUS; 196·71, WATTS. Melting point, 2192° Fahr. (1200° C.), POUILLET; 2518° Fahr. (1380° C.), GUYTON-MORVEAU; 2596° Fahr. (1425° C.), DANIELL; and 2264° Fahr. (1240° C.), RIEMSDIJK. Specific heat, 0·324; heat-conducting power (silver = 100), 53·2; electric conducting power (silver = 100) is, according to MATTHIESON, 55·19 at 72° Fahr. (21·8° C.).

This. the most precious of all those metals which have been found distributed in appreciable quantities over the earth's surface, has been deservedly valued from the most remote antiquity on account of its rarity, the richness of its colour, its non-liability to tarnish, and other valuable qualities. It never occurs in nature in a state of absolute purity, but can be so obtained artificially; and then possesses a rich yellow colour and high metallic lustre, but is nearly as soft as lead, being easily scratched by the nail. It would therefore in this state be unsuitable for the manufacture of articles of jewellery or for coinage. In malleability and ductility it exceeds all other metals, as it is capable of being beaten out into leaves one ten-thousandth of a millimètre ($\frac{1}{250000}$ inch) in thickness, and 1 grain of the metal can be drawn out into a wire 167 yards long. In tenacity, however, it is inferior to iron, copper, platinum, and silver. Its specific gravity is inferior only to that of platinum and a few of the rare metals, such as Iridium, Osmium, &c. Gold is found in nature almost always alloyed with other metals: the few compounds which are found—namely, *Sylvanite*, or telluride of gold and silver, and *Nagyagite*, or telluride of lead with gold, silver, and copper—being extremely rare. It is known also to exist in infinitesimal quantities in all galena, where, according to PERCY, it is most probably in the form of sulphide.

Historical Notice.—Numerous references to this metal occur in the Old Testament. Probably in consequence of its existing in the metallic state in the sands of rivers, it was the first metal known to man.

That the ancients were acquainted with the refining of the precious metals to a certain extent, plainly appears from different passages in the Old Testament, in which familiar allusion is made to this operation; and made, too, in terms which seem to imply that the methods then adopted were in many respects similar to those now employed. Silver and gold are purified or separated from foreign ingredients by much the same processes; a knowledge of the one implies a knowledge of the other; and JOB says, surely there is a mine for silver, and a place for gold, which men refine; while DAVID compares the words of the LORD to silver tried in a *furnace of earth*, purified many times. MALACHI is still more particular when, in comparing the Judge of all the earth to a refiner's fire, he says: *he shall sit as a refiner and purifier of silver, and he shall purify the sons of Levi, and cleanse them as gold and silver.* Here there is an evident allusion to the last operation required in the refining of silver—that of cupellation—during which the refiner must place himself at the furnace, and watch till the metal emits a bright flash, which indicates that the process is finished.

It is certain then that they were able to separate gold and silver from other metals, but it would appear also certain that they were unable to separate these two noble metals from each other; and this may account for the prevalent belief, that samples of gold from different sources possessed different qualities, although certain passages in the Bible may refer to the state of purity in which it is found.

Indeed, it seems probable that much of the gold in use contained a very large percentage of silver; and the gold from Ophir, Parvain, the north, &c., probably mainly differed from each other in the amount of this metal which they contained. It should be mentioned that one particular alloy, much employed in early times, and called *electrum*, is specially mentioned by PLINY as containing 4 parts of gold to 1 of silver; and this is the mean proportion in which the metals are found alloyed together in many auriferous localities. According to KLAPROTH, however, the *electrum* of the ancients consisted of 2 parts of gold to 1 of silver.

Although the process of extracting the precious metals by amalgamation is generally considered a Spanish invention of the sixteenth century, there is little doubt that the ancients were acquainted with the use of amalgam, both as a means of separating the noble metals and for purposes of gilding. This appears from PLINY, who lived about A.D. 50 (lib. xxxiii. cap. 6). VITRUVIUS also (lib. vii. cap. 8), who lived at the commencement of the Christian era, gives a very detailed account of the method of recovering gold by means of amalgamation, from cloth in which it had been interwoven; the amalgam being squeezed in a cloth, and the mercury in the resulting mass expelled by the aid of heat.

Although it can scarcely be supposed that the total amount of gold in circulation in ancient times was so great as at present, yet, from the practice of hoarding the precious metals which then prevailed, and from the limited commercial intercourse which then existed, it seems to have accumulated in some countries and in particular circumstances to an incredible extent. Conquerors were accustomed to carry off all the gold they could collect or extort from the subdued nations; and thus, after a series of successes, the coffers of the victorious monarch and his subjects became replenished with treasure. Hence the vast amount of the precious metals which poured into Rome from the provinces when she ruled the world. Hence also the enormous accumulation of gold and silver which King DAVID is recorded to have collected during his lifetime for building the temple—an amount which has been estimated at not less than nine hundred million pounds sterling, being more than all that has been raised in all the mines in the known world during the last fifty years. It is scarcely possible to avoid the suspicion that some error has crept into the calculations by which this

astounding result is arrived at; but still it is quite certain that immense quantities both of gold and silver were often accumulated in ancient times; and to this day no inconsiderable mystery hangs over the sources from which those treasures were derived. Any little knowledge that is possessed on this subject will be mentioned in enumerating the auriferous or gold-producing localities known at the present day.

It is probable that, with the decline of the Roman Empire, the art of extracting and refining the precious metals became to a great extent lost. Then, however, a new art began to appear, viz., alchemy, which aimed at two great objects, the discovery of a medicine capable of prolonging life, and the conversion of base into noble metals. The years of patient labour which many of the alchemists devoted to those *ignes fatui*, the elixir of life and the transmutation of metals, have resulted in many valuable incidental discoveries, and have contributed largely to prepare the way for the triumphs of modern chemistry. Hermes Thrismegistus, who is said to have lived about 1928 B.C., is generally quoted as the oldest of the alchemists; but there can be little doubt that the writings attributed to him are entirely spurious. This class of chemists cannot be said to have died out till about the end of the eighteenth century, the time of Priestley, Black, Davy, and Lavoisier; but even in more modern days it is frequently announced that the transmutation of the metals has been accomplished. Thus, in 1853, M. Theodore Tiffereau communicated to the Academy of Sciences of Paris a paper entitled "The Metals are not Simple, but Compound Bodies," in which he asserted that he had prepared gold by artificial means.

Reference should be made to a remarkable work on alchemy, attributed to Geber the Arabian, supposed to have lived not later than the seventh century. In it he mentions a medicine containing a solution of gold in nitro-hydrochloric acid. If the work be genuine, therefore—a point on which considerable doubt rests—aqua regia (a mixture of nitric and hydrochloric acids), the solvent for gold, was known in his time. It was certainly in use at the end of the fifteenth century, and was so named on account of its being the only liquid capable of dissolving gold.

The further history of gold, which has assumed a profound interest in modern times, and demands therefore a larger space than is usually devoted to historical notices in this work, will be given in connection with the sources or localities from which it is chiefly derived.

Sources.—With the single exception of iron, gold is more generally distributed than any other metal; but for the most part it occurs in such minute quantities as either to escape notice, or not to repay the cost of extraction. On the other hand, many localities in different quarters of the globe, and especially, of late years, portions of California and Australia, have proved splendid exceptions. The principal matrix of gold is quartz rock, and this rock is commonly a vein of greater or less thickness, intersecting beds of granite. The chief sources, however, from which gold is obtained, are firstly, alluvial deposits, and secondly, quartz rock. The former, consisting of sand and gravel, have been produced by the disintegration of the silicious, granitic, and other igneous and metamorphic rocks, and have been transported by the agency of water from the mountainous districts. In these beds it is invariably found in the metallic state, but is never quite pure; it usually contains a certain proportion of silver, and not unfrequently iron, copper, and small quantities of several other metals.

The quartz veins of a district are not usually worked till the alluvial workings are more or less exhausted, and always involve the employment of more powerful and extensive apparatus, as well as more skilled labour.

Herodotus states that the people living near the source of the Indus obtained a large quantity of gold from the eastern border of the great Bactriana, and the desert steppes of Cobi; and he also refers to productive mines in the north, the remains of which, on the south-eastern borders of the Ural mountains, are described by Pallas in his Travels, and were likewise visited by Lepechin and Gmelin. These ruined mines, which have all the marks of a very remote antiquity, are supposed to have been the work of a nomadic people, in all probability the Scythians. It is evident that much gold was produced in ancient times from the mines of Nubia and Ethiopia, which like those of the Uralian chain produced a copper-yielding gold. Belzoni discovered that a very extensive tract had been worked in the Sahara mountains, and from these sources the Pharaohs are supposed to have derived their wealth. Jacob, from a very close examination of the subject, is led to infer that not less than six million pounds sterling of the precious metal must have been produced annually from these mines.

There were rich silver mines in Attica; gold mines in Thrace, and in the island of Thasus. Thessaly produced ores which were rich in gold; and Epirus, rich silver mines. From these sources the Athenians drew their wealth.

The Romans obtained their treasures from various sources besides the conquered provinces—from Upper Italy, the province of Aosta, the Noric Alps, Illyria. From this district, at one period, gold was abundantly obtained, partly in large grains on the surface, and partly in mines, so pure that an eighth part only was lost in the processes of smelting and refining. Its great quantity caused a decrease of one-third in the price through all Italy, and induced the proprietors to employ fewer workmen in order to raise the value. The Tarbelli, a people at the foot of the Pyrenees, also streamed extensively for gold.

It is stated on the authority of tradition, that when the Phœnicians visited Spain, they found silver in such abundance, that they not only loaded their ships to the water's edge, but made their com-

mon utensils, and even anchors, of this metal—a statement which harmonizes with the representations given by the Spanish discoverers of Peru. But whether this account be exaggerated or not, it is certain that the Phœnicians lost no time in taking possession of the country, and forming colonies in the present Andalusia. Now it is known that Spain anciently possessed mines of gold in regular veins, especially in the province of Asturias. The Tagus and some other streams of that country were said to roll over golden sands; and there is little doubt, that when colonized by an active commercial people like the Phœnicians, its mineral wealth would be developed, and would contribute largely to the supply of the precious metals in the ancient world.

It is affirmed that the Romans extracted gold from the quartz lodes in Transylvania, and also at the Ofogan in Caermarthenshire in this island, during their occupation under Trajan. It is probable, however, that but little would be obtained from these sources; and not much further is known of the ancient gold working.

The principal workings known at the present day are those of Australia and New Zealand in the southern hemisphere; of California, the Appalachian Mountains, and British Columbia in North America; Brazil, New Granada, and Peru in South America; Bambouk, Kordofan, and Transvaal in Africa; the Ural Mountains in Siberia; and of Transylvania and Hungary in Europe. Gold is found, however, in smaller quantities in several other places; and it is proposed now to briefly indicate the various localities in which it is known to exist, considering more in detail the important fields of California and Australia.

Europe.—There are probably few countries without traditions of gold, and these have not been wanting in the British Islands, which have furnished from time to time small quantities, although seldom in sufficient amount to be equivalent to the cost of procuring it. Specimens are occasionally found in Wales, in the Cornish stream-works, and in different parts of Devonshire. These have been worked at intervals, but with the exception of one, the "Vigra and Clogau" mine, near Dolgelly, none have paid their working expenses. The total produce of this mine to 1869 was 13,947 ozs., whereas all the remaining mines in North Wales together only produced 1022 ozs. Fresh discoveries were made at Vigra and Clogau in 1866, in consequence of which the yield in 1867 rose to 1520 ozs. This, however, was soon exhausted, and since 1869 it has ceased to be productive. For a very complete account of the Welsh gold deposits, the reader may be referred to Ure's Dictionary, Article "Gold."

In Scotland it occurs at Leadhills and Cumberhead, in Lanarkshire, and Glen Turrit in Perthshire, but only in very small quantities; and quite recently (1874) discoveries have been announced in Buteshire and in Uist, an Island of the Scotch Hebrides. In the time of Queen Elizabeth extensive washings for gold were carried on in the alluvial soil of Leadhills. In the county of Wicklow, in Ireland, a considerable quantity of native gold was discovered towards the close of the last century, disseminated in a quartzose and ferruginous sand. This gold was chiefly found in *pepitas* or solid pieces, one of which weighed 21 ozs.; and so promising was the supply, that the peasantry in the neighbourhood of Ballinavalley river actually gathered in the course of two months an amount of gold for which ten thousand pounds sterling were paid. The extraction was then undertaken by government; but the supply was soon exhausted, for during the two years that the mines were in operation only 945 ozs. were obtained, which did not pay the necessary expenses, and the works were abandoned.

In France, the Rhone and other rivers present auriferous sands, but there are no workable mines in that country. It is probable that the deposits have been exhausted, like those of Spain, which were formerly rich and valuable, but are now neglected. So with the sands of the Danube and many other European rivers, which still contain gold in small quantities, but rarely worth the expense of washing. In the valley of the Rhine, between Basle and Mannheim, for example, gold occurs in flakes mixed with titaniferous iron; but so minute are the spangles, that it takes from 1100 to 1400 of them to weigh a grain troy. There are also auriferous sands in some rivers in Switzerland, such as the Reuss and the Aar.

In Sweden there is a mine at Edefors in Smoland, where the gold occurs native, and also in auriferous pyrites. Gold mines have been worked in the territory of Salzburg, amid the chain of mountains which separates the Tyrol and Carinthia. The yield per ton of ore in these districts is probably less than that in any portion of the globe, the mines at Zell, for example, averaging only about $\frac{4}{1000000}$ of the vein stuff. The mines of Salzburg have, in the last few years, much fallen off; thus, that at Goldberg of Rauris in 1871 produced only 14·1 lbs., while in other cases even less than this was obtained.

Bohemia many centuries ago produced considerable supplies of the precious metal, and washing was carried on at several places, the chief source being the mine of Eula, which is said to have yielded so largely that 734 golden images were made from its produce. The amount of gold found in Bohemia is now insignificant.

The ancients obtained large supples of gold from different parts of Italy, and, according to Strabo, the immense supplies decreased its value by one-third throughout that country. Now, however, the only important source is Piedmont, where veins of auriferous pyrites are found in the gneiss rocks at the foot of Monte Rosa; and although these ores contain only about 11 dwts. of pure gold per ton, they have long defrayed the expenses of working, and during the last few years they have been carried on under the management of English companies. Recently gold has been found to exist in Finland, and operations have been commenced in various localities; and the yield of this country during the summer of 1873 was about 150 ozs.

But the only gold mines of any importance in Europe are those of Hungary and Transylvania, the

former of which appears to have been worked as early as the eighth century; and these are not less remarkable for their position than for the peculiar metals with which the gold is associated.

They occur in several distinct localities, the gold being usually disseminated through sulphide of silver, which occurs, distributed in a partially decomposed feldspathic rock, at the Königsberg mines, while at those of Schemnitz and Felsobanya it is found with syenite or greenstone porphyry, also in the form of auriferous sulphide of silver. At Telkebanya the gold is extracted from a deposit of auriferous pyrites in trap-rocks of recent formation.

The gold found in Transylvania occurs in veins, varying in composition and frequently of great thickness, ranging from six to forty yards. Their walls are as a rule ill-defined, and the percentage of gold produced from the crude ore is but small. At Kapnik the gold is found in granite, associated with orpiment, while the mines of Offenbanya, Nagy-Ag, and Zalatna are especially worthy of notice on account of their yielding nagyagite and sylvanite, compounds of gold and tellurium—the only cases in which gold is found in combination.

It may be added, that the mines of Reichenstein, in Silesia, which had been abandoned for more than five centuries, and which only yield about 380 grains per ton of ore, have been opened with advantage, in consequence of the application on a large scale of a method invented by Professor Plattner for separating gold from the waste of arsenical pyrites, which will be described afterwards. These operations have, however, been discontinued, as all the old residues have been worked up; but the process is at present carried on on a large scale in California, under the name of the "Chlorination" process.

Asia.—The gold mines of Russia may be conveniently considered in this place, although existing both in European and Asiatic Russia. The Ural mines, including those of Berezovsk, near Ekaterinburg, extend through five or six degrees of latitude. Here there are deposits of partially decomposed auriferous pyrites disseminated in veins of quartz; and from these veins the precious metal is extracted by vertical shafts and lateral galleries. Generally, however, the gold is found associated with other metals, as platinum and palladium, in fragments or debris of auriferous rocks, mixed or disseminated at some yards' depth in an argillaceous loam.

In the days of Pallas, the gold alluvia of Russia were supposed to exist only near Ekaterinburg; but in the reigns of Paul and Alexander they were found to extend through several degrees to the north and south of that locality. It was only in the reign of Nicholas that portions of the great eastern regions of Siberia were found to be highly auriferous. In these districts the ground rises into low ridges, similar to those of the Ural, and like them trending from north to south. They are offsets from the great east and west chain of the Altai, which separates Siberia from China.

The chief auriferous districts are Perm, Tomsk, Oremburg, Irkoutsk, Yenisseisk, and the Kirghese. Towards the close of last century the Berezovsk mine produced about 8400 ozs. annually, but in 1850 the yield had fallen to 1200 ozs. troy.

The principal supply of Russian gold, however, is obtained by washing; and as labour is very cheap and water abundant, auriferous matter can be worked at a profit which in other localities would be valueless. In the Ural mountains, south of Miask, some rich sands were discovered in 1842, during the removal of certain old buildings, in which washing operations had been carried on. Under the corner of one of the buildings, at the depth of three yards, a mass of gold was dug up weighing 97 lbs. troy. This mass was placed in the collection of the Corps des Mines at St. Petersburg. The discovery of the rich sands was made at the same time; in the Ural districts the gold is not usually found in large lumps. It is commonly obtained in very small fragments, which are separated by washing; and the yield seldom exceeds 36 grains of gold per ton weight of soil. In the Altai auriferous district, which is represented to be as large as France, not only is the gold found mixed with sand and gravel on the surface, but considerable quantities are extracted by pulverizing the rocks. It is a remarkable fact that, not many years ago, the gold obtained from this distant region did not amount to a third part of that which the Ural district produced, whereas in 1843 the eastern tract yielded upwards of two and a quarter millions sterling, and the Ural produced little more than half a million.

The total produce of Russian mines up to 1870 is given as—

	Ounces troy
1814 to 1820.....	132,780
1820 " 1830,.....	878,400
1830 " 1840,.....	2,105,520
1840 " 1850,.....	6,647,460
1850 " 1860.....	8,244,300
1860 " 1870,.....	8,194,500
Total,.....	26,202,960

while the annual produce attained a maximum of 961,616 ozs. in 1847, and a minimum of 720,320 ozs. in 1852. The gold obtained from the 1126 gold diggings and mines which exist in Russia was, in 1871, 943,452 ozs. In the century previous to 1841 the mines of Berezovsk yielded about 392,000 ozs. of the precious metal.

It is evident, however, from the quantities existing in the East, that it must be extracted in considerable amount from various sources. It is found in the rivers of Syria and other parts of Asia Minor. The Pactolus, a small river of Lydia, is said to have rolled over golden sands, which were supposed to have constituted the origin of the proverbial wealth of Crœsus.

Thibet, according to an approximation of Jacob's in his "History of the Precious Metals," produces annually about 833 lbs. (troy) of gold. The amount now produced by India is inconsiderable in comparison with the large quantities which it must have formerly produced. Nevertheless, gold extracting has not altogether ceased in that country, for speci-

mens of Indian gold were exhibited at the recent International Exhibition held at Vienna (1873).

Africa.—This continent was most probably the chief source from which the ancients derived the greater portion of their immense supplies of gold, and many consider that Ophir is identical with the modern Zanzibar on the east coast. It should be mentioned, however, that in 1864 a traveller named Carl Mauch discovered several old workings in South Africa, in the high ground between the Limpopo and Zambesi rivers, where there was abundant proof that both gold and silver had been obtained on an extensive scale at a very early period. This, he considers, is certainly the original source of the gold brought in the ships of Tarshish, and possibly that from which it was sent to the ancient Ophir, in the Persian Gulf. The amount which Africa now produces annually is very small, being generally estimated at about £4000 (Birkmyre). This amount comes from mines in two different localities—those of Bambouk, south of Senegal, on the west coast, and those of Kordofan, between Darfur and Abyssinia, on the Upper Nile. In both these localities the gold occurs in spangles, chiefly near the surface of the earth, in the beds of the rivers, and almost always accompanied by a ferruginous earth or sand, nuggets of any magnitude never being found.

Gold is also said to have been discovered in Madagascar in small quantities, but the government prohibited its being worked, lest an influx of foreigners into the island should result.

Early in the year 1874 the first remittance of gold arrived in England from the newly discovered gold fields of Leydenburg, in the Transvaal Republic, Southern Africa, and there seems good reason to believe that this district will soon rival in richness the existing gold-producing countries. The climate, as is well known, is extremely healthy, and this newly opened-up country appears to offer a suitable field for emigration.

South America.—At the end of the last and beginning of the present centuries, the South American continent was the principal source of gold in the new world; but it has now sunk into comparative insignificance, in consequence of the vast quantities produced by California and Australia. Of the several mines in South America, those of Brazil are the most productive; the amount of precious metal extracted during the years 1752–1761 averaged about 19,000 lbs. annually, since which time, however, it has very much decreased. According to Walsh gold was known to exist here as early as 1543, the Indians having employed it for the manufacture of fish-hooks; but the first authenticated account we have of its actual *discovery* seems to have been in 1682, when the ferruginous sand in the valley of the Mandi, a branch of the Rio Dolce, at Catapreta, was found to be auriferous; since that time widely extended deposits of auriferous sands have been found at the foot of the great mountain chain which runs parallel with the coast from the fifth to the thirtieth degree of south latitude. The main sources of gold during last century were the alluvial deposits of nearly all the rivers, especially the affluents of the Francisco, deep mining being hardly ever resorted to. Now, however, since the former have become quite exhausted, mining is the sole method employed. The gold is not inclosed in well-defined veins, as is usually the case in rock mining, but disseminated in large beds.

The most important gold mine in Brazil is the Morro Velho Mine, belonging to the St. John d'El Rey Company, which in the interval from 1849 to 1865 produced over 58,000 lbs. troy.

The method of washing the ores, &c., practised in Brazil, will be described subsequently.

This metal is likewise found in many other parts of South America, on both sides of the great chain of mountains which runs parallel with the Western coast.

Peru, which is essentially a silver producing country has yielded considerable quantities of gold. Washing is almost the sole method adopted, and this is carried on by natives. The annual produce is supposed to be about 2400 lbs., but no accurate information is published. New Granada has produced considerable quantities of gold, where it has been obtained both by alluvial washing and quartz mining, but chiefly the former. Although it is certain that large quantities still remain unextracted, operations are totally suspended, as the work is said to be extremely unhealthy. The principal washings are in Antioquia and Veraguas; the total produce of the former between the years 1804 and 1848 having been estimated at nearly £41,000,000. Bolivia and Chili have long been known to be gold producing countries, but of these no information of a recent date is attainable.

North America.—More gold is now produced in the vast continent of North America than in any other part of the world. In this respect it has now taken the place which formerly belonged to South America, while the latter has sunk into comparative unproductiveness, less perhaps from the absolute exhaustion of the auriferous soils, than from the want of the capital and enterprise to work them successfully. North America was a gold-producing continent long before the discovery of the Californian treasures; but for many years the only source of this precious metal in that quarter of the globe was the argentiferous veins of Mexico, from which it was extracted along with the silver, as in the Peru mines of South America. At a later period, however, an extensive gold region was discovered in the United States, extending along the Eastern slope of the Appalachian mountains, from the river Rappahannock in Virginia southwards to the river Coosa, an affluent to the Alabama, which flows into the Gulf of Mexico. The metal is found in less quantity northward beyond Maryland to the state of Maine, nuggets, &c., only having been discovered at irregular intervals. In Canada and Nova Scotia, however, gold is met with in considerable quantities. The rocks through the whole Appalachian chain are very similar in composition, consisting of various kinds of slates alternating with bands of granite and syenite. Of the American states, Professor Whitney considered that North Carolina was likely to prove the most productive,

provided the mines were honestly worked. It cannot be said that any of them have been profitable, but Virginia yielded tolerably constant, though small quantities, up to the time of the late civil war, when all mining operations were interrupted.

Although as early as 1855 Dr. Dawson hinted at the probability of gold being found in Nova Scotia, there does not seem to have been any discovery made till 1860; but after this date claims were taken up and gold discovered in various localities in quick succession. Since 1865 the yield has averaged about 23,000 ozs. obtained from crushed quartz, containing about $15\frac{1}{2}$ dwts. of gold per ton. The greatest amount produced in one year was 27,314 ozs. in 1867, since which date the annual yield has gradually declined, and in 1873 it was only 11,852 ozs.

Most of the rivers of that portion of Canada which lies south of the St. Lawrence yield considerable quantities of gold, which, until quite recently, was obtained almost entirely from alluvial washings. The first important mining company formed there, the "Chaudière Gold Mining Association," exhibited at the 1857 Exhibition several specimens of native gold. But the produce of Eastern America and indeed of all parts of the world was quite eclipsed about the middle of the present century, when the first of those sources of gold in California and Australia were discovered, which, in 1865, were yielding together about 66 per cent of the total produce of the world. The immense value of these stores, the first opening up of which took place about 1847, may be inferred from the fact that while in the ten years preceding that date (1838-1847), the total produce of the United States was about 7,600,000 dollars, that in the ten succeeding years (1848-1857) was about 389,200,000 dollars. This estimate, moreover, it should be observed, takes no account of the gold taken direct out of the country, and of which no returns are accessible.

The first of these recent discoveries was made in 1847, when California, a hitherto-neglected and little-known region, lying at the most remote south-western limit of North America, rose into sudden importance as the El Dorado of the new world. The gold region, properly so called, occupies the northern part of California, commencing near the mouth of the Sacramento river, in lat. 39° north, and long. $122\frac{1}{2}$° west, to the north-east of the bay and town of San Francisco, from which it extends south and north. At this point two rivers unite and discharge themselves into the sea—the Sacramento flowing from the north, along a valley formed by mountain ranges, and the San Joaquim, flowing from the south, along a similar valley, inclosed on one side by the Rocky Mountains, and on the other side by the mountainous ridge which protects the western coast. It was on the property of an intelligent Swiss emigrant, Captain Sutter, who had become a wealthy settler on the banks of the Sacramento, that the first traces of gold were discovered in September, 1847. This happened in the course of the erection of saw-mills on the estate, when Marshall, the contractor for the building of these, observed glittering particles in the sand of the mill-race, which were ascertained to be gold; and on making further search, it was found that the precious metal was very extensively diffused in the bed of the stream. The discovery soon became known to the work-people, by whom the intelligence was conveyed to San Francisco, and in no long time the whole population of the little town, and the scattered and scanty settlers in the neighbourhood, abandoned their dwellings and occupations to engage in the exciting search. The supply exceeded the most exaggerated accounts that had been given; new and richer localities were discovered; the gold was found in the beds of various streams flowing into the Sacramento; in the mud of the river itself; in the channels of old water-courses, and along the sides of the hills. The intelligence rapidly spread to the neighbouring countries—to Mexico, to South America, to the United States, and thence to Europe. People began to flock from all quarters to the once neglected but now coveted region; it became, in a few short months, the scene of a considerable population, instead of a few scattered tribes of Indians; miners or diggers in parties spread themselves over the face of the country; and San Francisco, from a mere village, grew up into a place of wealth, importance, and stirring activity. It was at first very generally considered that the supply would soon fail, and although this has been by no means the case, yet it seems certain that the Californian fields are very gradually declining — the maximum produce having been about 65,000,000 dollars in 1853 as compared with the yield of only 31,500,000 dollars in 1872. In the former year the amount exported was 57,000,000 dollars, and in the latter it was 12,000,000 dollars. On the other hand, it should be remembered that the methods for extracting the precious metal have been so greatly improved that it is now found very profitable to re-wash the "tailings" or waste left by former miners.

For information upon the geology of California, we cannot do better than refer the reader who requires detailed information to the "Geological Survey of California," by J. D. Whitney, published by the Californian government.

The Sierra Nevada itself consists mainly of a central axis of granite, disturbed at intervals by volcanic action, in which is found only a small quantity of quartz. Along the western slope of this mass are thick bands of slates and shales, alternating with masses of serpentinous and trap rocks. The slates of this auriferous locality belong, according to Professor Whitney, to the Jurassic period, although in all probability some of those in Plumas county and elsewhere are of the Triassic. The great metallic belt lies on this western slope, commencing at about the Tejou pass, and extending to the northern limit of the state. These metamorphic slates are the true gold-bearing rocks, and form a belt about 300 miles long by 50 miles broad.

West of the Rocky Mountains the gold-bearing states are California, Nevada, and Oregon; together with the territories of Washington, Utah, Montana, Idaho, Arizona, Colorado, &c. These occupy in all

over a million square miles, though of course in this vast area there are large tracts of land in which gold has not yet been discovered. Gold occurs on the Pacific coast in three distinct forms, each requiring its own special mode of working. These are :—

(1) *Auriferous veins*, most frequently inclosed in metamorphic slates.

(2) *Deep placer diggings*, deposited by ancient river systems.

(3) *Shallow placer diggings*, deposited by present river systems.

Quartz Veins.—In California the gangue of the auriferous veins is invariably quartz, which is generally crystalline in structure, though sometimes partially vitreous. The veins are irregularly distributed among the metamorphic slates, but occur chiefly in the neighbourhood of crystalline and eruptive rocks. In the southern portion of the Sierra, an immense central quartz lead extends from Mount Ophir beyond Mokelumne hills, a distance of about 75 miles, and it varies from 6 to 60 feet in thickness. In the neighbourhood are several small quartz veins, running more or less parallel. There is, however, a distinct break between the southern and northern veins, these latter being more numerous, but individually less in extent. The quartz of a veinstone is generally ribboned, so as to form a succession of layers parallel to the walls of the lode, and frequently some one or more of these laminæ are more productive than the rest. The metallic minerals, ordinary iron pyrites, blende and galena, and less frequently arsenical pyrites, magnetic and copper pyrites, and cinnabar, usually exist in the gangue, and are invariably accompanied by gold. Indeed, so much is this the case, that, according to Phillips, veins are not regularly productive which do not contain some one or more of these substances.

Placer Diggings.—About two-thirds of the whole gold produce of California is obtained from these alluvial deposits, the remaining one-third being the result of quartz mining. The attention of the first miners was directed entirely to such sources of gold as were near the surface, and therefore easily accessible to ordinary tools, and immense sums were obtained by this means. But as these superficial layers became gradually exhausted, machinery was introduced and deposits of a more ancient date were profitably worked. The former, or "shallow placers" were formed at a more recent period than the latter, "deep placers," which were deposited by an entirely different river system to that now in existence, which evidently flowed at a much higher level and frequently at right angles to the valleys of the present day. These apparently unlimited deposits are now worked on a gigantic scale by what is known as the "hydraulic process," described subsequently, which performs its work so rapidly and economically (provided there be an abundant supply of water) that gravels containing only 7 cents per cubic yard can be worked with profit. Although gold is disseminated through the whole mass, it always collects in the greatest quantities at the bottom on the shelf or *bed rock*, where at times the richness is remarkable. Thus at Mokelumne Hill, Laur states that in consequence of the richness miners were prohibited from possessing more than 15 square feet, no less than 250 lbs. weight having been known to be extracted from this space. The amount obtained, however, varies considerably, and seems to be chiefly dependent on the form of the surface of bed rock; thus, if it be rounded and convex upwards there is not likely to be a large deposit, whereas a maximum produce may be expected when the reverse is the case. These deep placers are frequently covered by a layer of of lava, and Newberry concludes from an examination of the leaf beds, &c., found in those of a more clayey nature, that they belong to the Tertiary age, and are most probably of the later Pliocene epoch.

Phillips (in the "Proc. Roy. Soc." for 1868) gives the following as the result of his examination of the geology of California, regarding it from a chemical point of view :—

(*a.*) Quartz veins have generally been produced by the slow deposition from aqueous solutions of silica on the surfaces of the inclosing fissures.

(*b.*) From the general parallelism with its walls of the planes of any fragments of the inclosing rock which may have become imbedded in a vein, it is to be inferred that they were mechanically removed by the growth of the several layers to which they adhered, and that a subsequent deposition of quartz took place between them and the rock from which they had become detached. In this way were introduced the masses of rock known as "horses."

(*c.*) The formation of quartz veins is due to hydrothermal agencies, of which evidences are still to be found in the hot springs and recent metalliferous veins met with in various parts of the Pacific coast.

(*d*) From the variable temperatures at which the vacuities in their fluid cavities become filled, it may be inferred that they are the result of an intermittent action, and that the fissures were sometimes traversed by currents of hot water, whilst at others they gave off aqueous vapour or gaseous exhalations. This is precisely what is now taking place at Steamboat Springs, where the formation of a vein is in progress, and from which currents of boiling water are often poured forth, whilst at other times the fissures give off currents of steam and heated gases only.

(*e.*) That gold may be deposited from the same solutions which give rise to the formation of the inclosing quartz, appears evident from the presence of that metal in pyrites inclosed in silicious incrustations, as well as from the fact of large quantities of gold having been formed in the interior of the stems of trees, which in deep diggings are often converted into pyrites.

(*f.*) The constant presence of iron pyrites in auriferous veins, and when so occurring its invariably containing a certain amount of gold, suggests the possibility of this sulphide being in some way necessarily connected with the solvent by which the precious metal was held in solution. It has been shown that finely divided gold is soluble in the sesqui-

chloride of iron, and more sparingly in the sesquisulphate of that metal. It is also well known that iron pyrites sometimes results from the action of reducing agents on the sulphate of that metal. If, therefore, sulphate of iron, in a solution containing gold, should become transformed by the action of a reducing agent into pyrites, the gold, at the same time being reduced to the metallic state, would probably be found inclosed in the resulting crystals of that mineral.

(*g*.) The silica and other substances forming the cementing material of the ancient auriferous riverbeds have probably been slowly deposited at a low temperature.

It would be impossible here to give anything approaching to even a summary of the many gold-producing districts of California, for which the reader may be referred to the "Geological Survey of California," or to Phillips' "Mining and Metallurgy," to which we are indebted for much of the information given above. Mention must be made of two or three of the most important sources of the precious metal.

The centre of quartz mining is Grass Valley, in Nevada county, one of the most prosperous towns in the state. In 1865 the quartz mills there produced about 3,500,000 dollars worth of gold, the veins, although not large, being extremely rich. The total yield of this district from its opening in 1849 to 1872 is said to be about forty million dollars. This county also possesses several extensive hydraulic washings, second only to those of Sierra county, where exists the famous *Blue Lead*, a deep placer of the Pliocene Tertiary period, remarkable for its richness, and for the fact that it runs in a direction at right angles to the rivers of the present day.

It should be mentioned, however, that in a government report on the "Mines and Mining west of the Rocky Mountains," A. Bowman states that "the 'Big Blue' Lead is a myth, passing through every miner's claim where there is deep gravel." He further observes that, "after devoting considerable pains to the collecting of facts for the determination" of the truth of the generally-accepted statement with regard to the ancient rivers being at right angles to those of the present day, he has arrived at the conclusion that "the Pliocene rivers have not varied at all in the general course from that of the present rivers."

The yield of the other states and territories mentioned above is inconsiderable in comparison with that of California. Among them Colorado, Idaho, Oregon, and Montana have been most productive; and in the recent Exhibition at Vienna (1873) specimens of tellurium gold from Nevada were exhibited.

British Columbia and Vancouver's Island should be noted, as they promise to afford a continuous supply of the precious metal. The former contains immense auriferous districts, situated on the banks of the Fraser and Thompson rivers, from which gold is obtained by washing. During the last fifteen years British Columbia produced an amount valued at about forty-five million dollars, while annually about 130,000 ozs. are obtained.

Australia.—It is a well-ascertained fact, that although the gold-fields of California were not really discovered and worked till 1848, yet on a small scale quartz mining was carried on there as early as 1843. Similarly in Australia, the great excitement on the subject did not take place till long after the first announcement of the existence of gold; but when washing operations did commence, they soon gave every promise of equalling those of California. The first known discoveries of the precious metal were made independently by Count Strzelecki in 1839, and the Rev. W. B. Clarke in 1841, each of whom communicated the fact to the governor of New South Wales, who, however, advised that the existence of gold in the country should be kept secret, lest it should militate against the interests of the colony; the reason he assigned being, that it would be impossible to maintain order among the 45,000 convicts then in the colony.

It is also especially interesting to note that so early as 1844, and without having heard of the discoveries made by Count Strzelecki and Clarke, and without even ever having visited the country, Sir Roderick Murchison, by comparing the maps of the mountain ranges with those of the Ural mountains, "publicly asserted the high probability of the existence of gold in Australia. This bold induction was based upon his knowledge of the geological formation of that country; and the wonderful results of gold mining in Victoria and New South Wales afford a proof of scientific sagacity almost unparalleled in the history of science."

To E. H. Hargreaves, however, is due the honour of having really discovered gold in remunerative quantities. He was struck with the general resemblance of the mountains of Australia to those of California, and at once proceeded to search for the precious metal, which he very quickly discovered in considerable quantities. In April, 1851, he addressed a letter to the colonial secretary announcing that he had discovered gold at Summer Hill Creek and other places near Bathurst, which is situated about 150 miles west of Sydney, New South Wales.

Scarcely had this communication been made to government, when the discovery became generally known through some persons who had been employed under the directions of Hargreaves. The fact was divulged that on the 8th of May these persons had obtained several ozs. of gold at Summer Hill Creek; and on the 13th of the same month great excitement was created by the report that a solid piece, weighing 13 ozs., had been found. This, on inquiry, proved to be correct, and hundreds of persons immediately left their accustomed avocations and started for the *diggings*, as they were now called. The excitement rapidly extended, and on the 19th of May 400 persons were congregated at Summer Hill Creek; on the 29th, 1000; and on the 5th June their numbers had increased to 1500.

A few weeks subsequent to these discoveries in New South Wales the precious metal was found to exist in Victoria; and as these fields have since proved to be by far the most productive in the

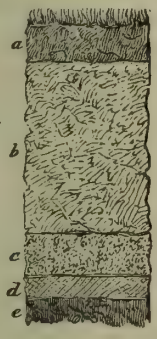
country, we will notice them first. Gold is known to have been found in small quantities by the settlers long before the announcement was made in 1851. Immediately on this, however, there was a great rush to the diggings, causing great inconvenience to society in suddenly producing a rise in the price of labour and provisions. From the researches of Selwyn, the government geologist, it appears that the gold-bearing strata of Victoria belong to a geological period much more ancient than that of the auriferous rocks of California; they belong, in fact, to the lower Palæozoic or Silurian epoch, and are, as Sir Roderick Murchison observed, almost identical in character with the Uralian mountains.

These rocks of Victoria are remarkable for "the almost total absence of limestone bands, the number and extent of the quartz veins, and the constantly recurring protrusions, at short intervals, of granitic, and occasionally of Plutonic trappean rocks." The quartz veins vary in thickness, from that of a sheet of paper to many feet; the thick veins being found in the lower portions of the series, but they are as a rule less productive than the thinner ones in the upper beds. The mines are frequently worked to immense depths, the deepest at present in existence being the "Magdala" mine, having a depth of no less than 1225 feet. Although the metamorphic rocks of Victoria appear to belong to a more ancient geological epoch than those of California, it should be observed that the drifts or deep diggings of the two countries seem to belong to the same geological epoch, and are both covered by a volcanic mass. Selwyn has concluded that there must exist two distinct series of quartz veins; the older ones having been formed previous to the Miocene period, and being comparatively barren; while the newer ones, formed subsequently, but previous to the Pliocene period, are productive. Gold is obtained in Australia from three sources, the quartz veins, the deep placers, and the shallow placers, as in California, and according to R. B. Smyth it is now found to exist in the claystone itself. In the earlier days of the colony digging was the sole method resorted to, but now this is gradually giving way to quartz mining.

Fig. 1.



Fig. 2.



The gold is frequently found at the surface mixed with the sands of rivers, but the auriferous stratum is generally buried at considerable depth, and hence the necessity of opening *pits* or *diggings*. Figs. 1 and 2 will afford some idea of the Australian gold-field strata. The latter represents what the diggers call a surface gullet, the gold being met with at about 16 feet from the surface; the former is a section of a deep gullet, in which the auriferous ore is at a depth of 36 feet. The corresponding letters in both sections indicate similar strata: *a*, black loam and quartz; *b*, white loam, clay, and sand; *c*, brown clay; *d*, gold layer; *e*, yellowish-brown rock; *ff*, quartz in a concrete mass; *g*, stratum of sand; *h*, common clay. The auriferous ore earth is generally of a light colour, or largely mixed with quartz pebbles, very tenacious and difficult to wash. It lies upon a yellowish-brown rock, of a rotten texture, known as fixed slate, whilst higher up, above the gold, the strata presents igneous features.

The whole of the auriferous region of Victoria is divided into six districts, named after the chief town in each. These are—Ballarat, Castlemaine, Sandhurst, Maryborough, Beechworth, and Ararat; the two most important fields being Ballarat and Bendigo, the latter of which is situated in the Sandhurst district. As with nearly every gold field, both were originally famous for their shallow placers; but these having been long since exhausted, the precious metal is now extracted entirely by quartz mining.

The methods of extracting the gold will be described subsequently. Meanwhile, however, it should be mentioned that they differ materially from those usually adopted in California, in consequence of the great scarcity of water in Australia in comparison with the inexhaustible supplies of that country. Phillips tells us that in the early days of quartz mining the raising and washing cost no less than £4 per ton; whereas now, in consequence of the introduction of machinery, the same work is done at 16*s.* 4*d.* per ton, thus enabling the miners to extract at a profit the gold from far poorer vein stuff than formerly.

From a geological point of view, the gold fields of New South Wales are very similiar to those of Victoria, but their produce is considerably less—the annual amount averaging only about 500,000 ozs., whereas that of the latter country is generally about 2,000,000 ozs.

South Australia, Queensland, Tasmania, and New Zealand, especially the latter, are all gold-producing countries; and about the year 1861 considerable excitement was caused by discoveries being made in the beds of the various rivers of New Zealand. Up to 1873 North and South Islands together have yielded nearly seven million ozs. Further information relative to the produce of this and other countries will be given at the close of the present article, under the head of statistics.

Origin and Position of the Gold Deposits.—Auriferous rocks, in whatever part of the world they be found, almost always exhibit a striking resemblance to each other; and although at times gold is discovered with granite, &c., as a matrix, it is generally associated with quartz. Indeed, so universally is this the case that, as has been already mentioned, Sir R. Murchison, on observing the identity of composition of the

Ural Mountains and the great auriferous chain of Australia, announced that gold would ultimately be discovered in that country. These rocks are of the Silurian period, and it has been observed that the richest deposits are found where rocks of this age have been disturbed by volcanic action. Referring to this subject, Sir Roderick remarks that "the most usual original position of gold is in the quartz ore veinstones that traverse altered Palæozoic slates, frequently near their junction with eruptive rocks. Sometimes, however, it is also shown to be diffused through the body of such rocks, whether of igneous or of aqueous origin. The stratified rocks of the highest antiquity, such as the oldest gneiss or quartz rocks, have very seldom borne gold; but the sedimentary accumulations which followed, or the Silurian, Devonian, and Carboniferous (particularly the first of these three), having been the deposits which, in the tracts where they have undergone a metamorphosis or change of structure by the influence of igneous agency or other causes, have been the *chief* sources whence gold has been derived."

Following up these conclusions, a writer in the *Quarterly Review* has pointed out that the mountain ranges bordering on the Pacific are all auriferous. Thus the great gold fields of Australia extend without interruption along the slopes of the range separating the eastern seaboard from the Continent, while the gold-bearing mountains of California and British Columbia extend in an unbroken line along the western shore of America. Indeed, the American auriferous districts extend along the whole coast-line from Behring's Strait to Cape Horn, while the Australian range extends southward across Bass's Straits, and northward it crops up at intervals in the various islands, finally terminating in Japan. Thus it will be seen that the great basin of the Pacific has on each side an elevation of volcanic origin, from which at intervals gold is obtained. The fact of the auriferous districts only occurring at intervals is explained by Sir Roderick Murchison's hypothesis already referred to—namely, that the most auriferous rocks are of the Silurian age, and that the most usual original position of the metal is in quartzose veinstones that traverse altered Silurian slates, frequently near their junction with eruptive rocks.

It should be mentioned that Professor H. Wurtz differs from Murchison as to the origin of gold, and has suggested a very plausible theory, ascribing it to a totally different cause. Having observed that aqueous solutions of sulphate of sesquioxide of iron were capable of retaining in solution a small but appreciable amount of metallic gold, and coupling this with the general belief that gold and gold-bearing sulphurets have been of aqueous deposition, he suggests that all the gold was held in solution in a "Prozoic thoroughly oxidated ocean," the sulphurets of iron now so abundant in crystalline rocks being dissolved in it as persulphates, and this persulphate in its turn being quite capable of retaining in solution all the gold of the earth's crust. When, however, in this lifeless ocean organic existence commenced, together with the accompanying deoxidizing processes, the ferric became ferrous salts, and these being incapable of retaining gold in solution, it was deposited. Wurtz refers to one of the two richest gold fields yet discovered—that of California—as disproving Murchison's general conclusion, that all gold fields are of the Lower Silurian age, this formation being as recent as the Jurassic.

Method of Examining Auriferous Deposits.—As a general rule, the rocks in the district to be examined for gold should be either granitic, porphyritic, or quartzose, although it is also found in other formations, and particularly in clay-slate. The auriferous quartz is often stained of a rusty brown colour, from the presence of peroxide of iron, and in many instances presents a cellular or honeycombed appearance. The points to be most carefully examined are the sands of the rivers and streams, or old water-courses, as well as the particles of disintegrated rock which often accumulate in the eddies of ravines formed on the sides of hills by the action of water during great floods. The sections of rock exposed by this action must also be examined with a view to the discovery of veins of auriferous quartz, from which specimens are broken off and afterwards carefully assayed.

The method of conducting a systematic assay of gold ores and alloys will be fully explained afterwards. It is a somewhat tedious and difficult process, requiring considerable experience and a regular assortment of apparatus. But even in the absence of these, a tolerably correct estimate of the amount of gold present may be readily arrived at by the following simple method.

The first and most important object must be to obtain a small sample which can be relied upon as fairly representing the composition of the mass. This, indeed, is the most difficult part of the process, and can only be secured with any degree of certainty by taking large quantities from different parts of a heap of the alluvial deposits or auriferous rock, the ore in the latter case having been previously broken up into small lumps of the size of beans. These having been thoroughly incorporated, a sample of a few pounds weight is taken, and for very rough estimations it may be sufficient to wash it with the pan, repeating the process until such a quantity of gold is obtained as can be easily weighed; this is then amalgamated with as small a quantity of mercury as possible, which is expelled by heating in an iron retort. The resulting gold is then weighed, whence we have sufficient data to determine the weight of gold per ton, thus:—

Let g be the weight of gold obtained in grains, G, the weight (in troy ounces) per ton, and p, the weight of sample in pounds.

$$\text{Then } G = \frac{14}{3} \cdot \frac{g}{p}.$$

expressed in ounces troy per ton avoirdupois. Of course, the above method will estimate all the silver, &c., contained in the ore as gold, and when a more accurate estimate is required assaying must be resorted to, which process will be described farther on.

The limit in the amount of gold found in river sand, beyond which it is considered impossible to work it at a profit, varies in different localities, and depends on the perfection of the apparatus employed, as well as on the cost of labour, &c. The following table enumerates several qualities of the sands of a number of rivers, together with the authorities:—

Locality.	Authority.	Relative Richness of Sand, &c.				
		1st. Quality.	2nd. Quality.	3rd. Quality (Average worked).	Least workable.	Average of unworkable gravel.
River Rhine.....	M. Daubrée,	0·000000562	0·000000243	0·00 000132	0·000000120	0·000000008
River Eder (Westphalia),.....	M. d'Eschwege,	0 000000390	0·000000222	0 000000130	—	0·000000016
Siberia,.....	Humboldt,	0·000006000	—	0·000002600	0·000001000	0·000000650
Chili,.....	Domeyko,	0·000078080	—	0·000009760	—	0·000001000

It will be seen from this table that the average unworkable gravel in Chili contains 1 part of gold in a million, and even this is nearly twice as rich as the best sand obtained on the Rhine, while it is 7·65 times as rich as the average sand worked on that river. M. Daubrée in 1846 read a paper before the French Academy of Sciences on the subject of the gold in the alluvial deposits of the Rhine, and he considers that with more perfect apparatus it could be worked at a profit, even if it contained less than what is given above as the "least workable" amount. With a view to converting the above decimal compositions into grains per ton, it may be useful to state that 1 part in a million is the same as 15·68 grains per ton.

Substances often Mistaken for Gold.—Though gold, in its separate and pure state, is readily distinguishable from other metals and minerals, by its colour, softness, high specific gravity, and insolubility in the simple acids, yet in the mixed state in which it is generally found it requires an amount of chemical skill to apply these tests; and hence, when glittering particles of other minerals appear, they are often mistaken for gold, even by persons who are not entirely ignorant of its characteristics. The substances which most generally lead to this mistake are iron pyrites, copper pyrites, and yellow mica.

Common iron pyrites, or *bisulphide of iron*, which is more frequently mistaken for gold than any other substance, occurs in small cubical crystals, in veins disseminated in the various slate rocks, and in the coal measures. It is of different shades of brass yellow, and often in fact contains minute traces of gold, though seldom a sufficient amount of that metal to render its extraction profitable. It may be readily distinguished from gold by the application of the magnet, as well as by the following characters: first, instead of flattening like gold under the hammer, it is extremely brittle, and therefore readily broken; second, its weight or specific gravity is only about one-fourth that of gold; and lastly, when heated with nitric acid it is dissolved with evolution of copious red fumes, whilst gold, when so treated, remains unaffected.

Copper pyrites, or *yellow copper ore*, the second mineral which is frequently mistaken for gold, may be considered as a compound of two equivalents of sulphide of iron, and one equivalent of sulphide of copper. This is the ore from which the largest proportion of the copper of commerce is derived. It occurs in a variety of forms, its primitive crystal being the regular tetrahedron. It is formed in lodes or veins, which usually occur either in granite, grauwacké, or clay-slate, and has a strong metallic lustre and deep brass yellow colour. It may readily be distinguished from gold by the circumstance that when heated on a piece of charcoal before the blowpipe it loses this yellow colour, and fuses into a dull black globule, which, from the presence of the iron, is magnetic. If mixed with carbonate of soda and a little borax, it yields, when similarly treated in skilful hands, a button of metallic copper. But an easier method to determine the presence of copper is to pulverize the ore in an iron mortar, or with a heavy hammer, dissolving the powder thus obtained in nitric acid, and evaporating the solution nearly to dryness; water is then added, and afterwards ammonia in excess, when, if copper be present, the liquor assumes a rich purplish colour, an unmistakeable sign of the presence of this metal.

Another method for determining the presence both of iron and copper, is to take some of the scoria left after submitting it to the blowpipe, and putting this in a test-glass, to pour over it a few drops of hydrochloric acid, when an effervescing solution will be obtained. A little of this liquid is then transferred to another glass—the one to be treated for iron, the other for copper. Into one of the glasses introduce a few drops of ferrocyanide of potassium, and liquid ammonia into the other. If iron is present, the liquid in the glass to which the ferrocyanide has been added will become blue, the iron combining with the ferrocyanogen, and producing Prussian blue. If copper is present in the same glass, but no iron, the liquid will become of a reddish-brown tint, ferrocyanide of copper being formed. If iron and copper are present together, the two metallic precipitates will be the result, and a purple tint arises from the mixing of the red and blue colours. The liquid in the glass to which ammonia was added will be changed to a brownish tint if iron is present, and to a fine blue if copper is there.

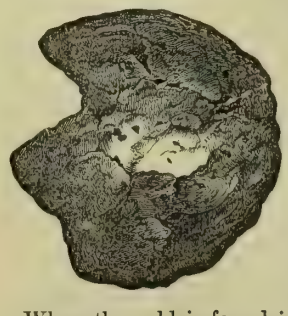
Mica, the third substance often mistaken for gold, is one of the constituents of gneiss, granite, and mica slate, and gives to the former its lamellar structure. In 1853 great excitement was produced at the Cape of Good Hope, in consequence of the discovery near Simon's Bay of a substance said to contain a large

proportion of gold. A quantity of this suspected mineral was sent home for analysis, and was found to possess a glistening, yellow, semi-metallic lustre; but when examined by the microscope its metallic brilliancy disappeared, especially when viewed by transmitted light. It had then a darkish-grey colour, being in thin semi-transparent plates. It was not acted upon by nitric or nitro-hydrochloric acid; and hence, doubtless, arose the error in taking it to be gold. In reality, it was nothing but mica, highly coloured with the oxide of iron.

The specific gravity of mica never exceeds 3·00; and this circumstance, together with its foliated structure, is quite sufficient to distinguish it from gold, which it somewhat resembles in colour; but even in this latter particular the microscope will dispel the illusion.

Characters of Native Gold.—Gold, as already stated, almost always occurs in the metallic state, generally in small grains or scales known as *gold dust*, sometimes in particles so minute as to be invisible, but occasionally in pieces of considerable weight, termed *nuggets*. It appears doubtful, indeed, whether, when this metal occurs in pyrites, it exists in every instance in minute metallic particles, or whether, in some cases at least, it may not be present in combination with sulphur. The auriferous pyrites, as Dumas remarks, contain the gold diseminated through their mass in such small quantities, that it is almost always impossible to ascertain, even with the aid of the microscope, in what state the precious metal exists. As a preliminary roasting of this auriferous ore is generally useful, with a view to the subsequent amalgamation, a doubt may be entertained whether it is really present in the metallic state, though this has been generally assumed hitherto. But Dumas thinks that the powerful electro-negative tendency of sulphide of gold affords a strong presumption in favour of the hypothesis, that this metal may exist partly, or even entirely, under the form of double sulphide, in iron and copper pyrites, &c. Brongniart observes, that it is chiefly in its association with these sulphides, as also with galena or sulphide of lead, blende or sulphide of zinc, and mispickel or arsenical pyrites—a sulphide of arsenic and iron—that the gold becomes invisible to the eye, a circumstance which is justly regarded as strongly confirming the opinion expressed by Dumas. The other minerals with which it is found associated are grey cobalt, lithoidal manganese, native tellurium, malachite, sulphide of silver, red silver, and sulphide of antimony.

Fig. 3.

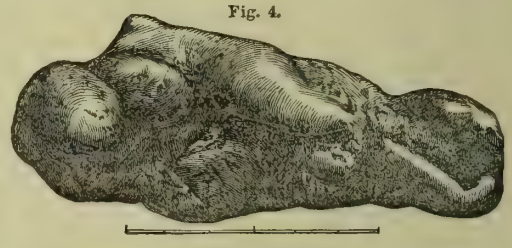


When the gold is found in the form of nuggets, these generally appear to have been melted, and resemble drops of melted metal poured into sand, the indentations being visible even upon the smallest particles of the gold when microscopically examined. It is certain that such indentations may be observed in most specimens, as indicated in Fig. 3, which exhibits a microscopic view of a fragment of Australian gold magnified seven hundred times.

J. B. Jukes, however, who may be regarded as a competent authority, conceives that this is probably a mistake, and that the idea may have originated from the gold having been deposited in small holes, crevices, and interstices of the quartz rock, and subsequently rolled, so that it assumes such forms as melted lead is seen to do. It does certainly appear remarkable that the particles of gold should retain indentations received in a state of fusion, after being tossed about, probably for a long period, among water and gravel.

Fig, 3 is a greatly magnified representation of a very small grain. Fig. 4, on the contrary, is a much reduced delineation of a lump of almost pure gold, weighing 27 lbs. 6 ozs. 15 dwts., which was found in the diggings at Forest Creek, Mount Alexander, in the colony of Victoria. Among other pieces brought home with it were several nuggets

Fig. 4.



SCALE OF SIX INCHES.

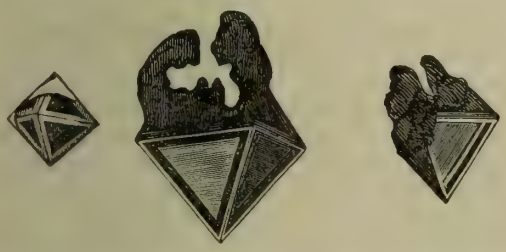
weighing upwards of a pound each, and one of 1 lb. 8 ozs. 6 dwts. These smaller lumps, however, contained quartz, whilst the larger one appeared a massive lump of nearly pure gold, of a very fine colour. It measured 11 inches in length by 5 in breadth, at the widest part. This was supposed to be the largest nugget which had been found in Australia up to the time of its discovery, but one or two others considerably larger have been since obtained.

Gold is also occasionally, though rarely, found in a crystallized state; and when met with the crystals should be carefully preserved as cabinet specimens, for which purpose their value is much greater than that which they are intrinsically worth for the gold they contain. The most common forms are the cube and octahedron, with their various modifications. The faces are generally dull, and in most instances the edges are slightly rounded. Some years ago several interesting specimens of crystallized gold from California were described in *Silliman's American Journal*, by Francis Alger of Boston. The collections in which the specimens were found were brought from California by G. E. Tyler of Boston, and H. B. Platt of New York. The crystals were distinctly octahedral, simple and modified, the surfaces being but slightly disfigured by attrition, or the effects of transporting action—a very unusual circumstance, as

gold is generally found in comparatively minute grains, at a distance from the rocky matrix in which it is supposed by some to have been primarily embedded. ALGER states in his paper, which was read before the Boston Society of Natural History, that he had never before seen what was unquestionably a genuine crystal from California. He adds that an irregular crystalline plane could only occasionally be traced out in former specimens; but among those exhibited were examples of crystallization as perfect, among the small ones especially, as are to be seen in magnetic iron ore or in spinelle.

Of the larger specimens in these collections, the most striking examples were three octahedra of the sizes exhibited in Figs. 5, 6, 7. Each of these crystals was found in an isolated state. The smallest one—Fig 5—was the most perfect, and was entirely free from any adhering portion of the matrix. This unusually perfect crystal exhibits, as partly shown in the Figure, four pretty regular faces in the lower half, and three of its six solid angles are perfectly formed to a point. Two of its faces are sunk or depressed; and in one of them the cavity thus formed is very deep and regular, like an interior triangle, the depression extending not quite to the edges, but so as to leave all round a narrow ridge or border, the interior sides of which are parallel with the edges of the crystal. ALGER inferred

Fig. 5. Fig. 6. Fig. 7.



that this depression, which is shown by a darker shade in the wood-cut, had been formed when the crystal was in a liquid state, and that, soon after the outside had congealed or solidified, the inner portion, or a part of it, had run out, leaving the surrounding consolidated edge in a perfect form. He remarks that he has seen something similar to this formed among artificial crystals, as, for instance, metallic lead—which takes the form of an octahedron—and lead ore partially desulphurized, when the metal was allowed to flow off slowly, just as the outer crust had formed over the surface of the crystals. Indeed, this parallel case is not of unfrequent occurrence in the crystallization of the ductile metals.

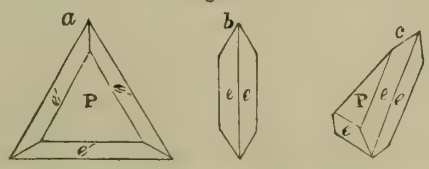
In the largest (Fig. 6) of these three crystals it will be observed that only one-half of the octahedron is formed, its base blending with the rough gold, or showing only the commencement of the planes of the upper pyramid. Three of the planes are quite smooth, except along their edges, which are permanently marked by the same projecting border or edge described as on the smaller crystal. The depression, however, is not so great as in the latter. ALGER remarked that this peculiarity was confined to the unmodified crystals.

In some there was a double series of these ridges, the inner one appearing to exhibit the commencement of another crystalline face within the cavity of the larger one. This phenomenon was strikingly shown in a crystal represented of the natural size in Fig. 7.

The two larger crystals (Figs. 6 and 7) were obtained from the collection of PLATT, who resided a couple of years at San Francisco, and being in a situation which brought him into constant intercourse with persons returning from the mines, purchased, at no small expense, the most interesting specimens he could find. His collection was described by ALGER as of singular beauty and value, comprising a great variety of ramified, arborescent, dendritic, and other imitative forms, all of these forms being sometimes fantastically joined together in the same specimen. In obtaining his valuable collection, he had selected from gold to the value of more than four millions of dollars. The remarkable size of the two larger crystals described, and the fact that some of the others contained oxide of iron, induced a suspicion that the greater part of them were pseudomorphs of sulphide of iron; but ALGER believed that they were formed under the ordinary circumstances of crystallization, either in an open space or while surrounded by a matrix, in such a fluid state as to allow them full freedom to take their natural form. His reasoning on the subject, if not perfectly conclusive, leads to a strong presumption in favour of the octahedron as the primary form of gold; and if this were more generally known, much disappointment and trouble might be saved in cases where sulphide of iron and other crystalline metallic forms are mistaken for the precious ore.

In TYLER'S collection ALGER found several rare modifications, some of them resembling those which come in their most perfect forms from Brazil. Fig.

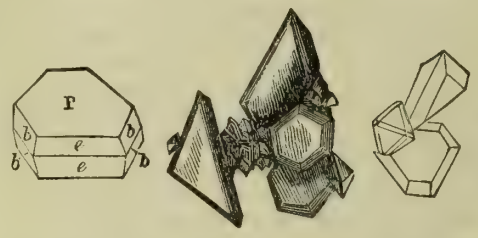
Fig. 8.



8 exhibits in three positions, *a*, *b*, *c*, a compound form produced by the union of two opposite segments of an emarginated octahedron. Fig. 9 is a modification of the same form, though apparently consisting of irregular six-sided tables, with truncated edges. Some of the unmodified macles, as shown in different positions in Fig. 8, were stated by ALGER to be very distinctly formed, the edges between *e e*, uniting the two segments of the octahedron, being well defined. This is very strikingly shown in Fig. 10, in which the crystals are shown magnified to twice their natural size. Fig. 11 shows the opposite side of the same specimen, connected with two other crystals, one a very beautiful and smooth-planed octahedron with emarginated edges.

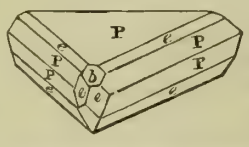
Fig. 12 exhibits a macle of gold which came from Malto-Grosso, in Brazil, and is in the collection of

Fig. 9. Fig. 10. Fig. 11.



the School of Mines, Paris. It is similar to that represented in Fig. 8, from which it only differs in exhibiting more of the planes of the octahedron and dodecahedron. This figure is copied from the volume of crystallographic illustrations accompanying M. Dufrénoy's treatise; but besides conforming his lettering to the notation of Phillips, those are made primary planes which are given by Dufrénoy only as secondaries of the cube.

Fig. 12.



In all these the octahedral form is manif st, which may therefore be assumed to be the form natural to gold when its particles crystallize in cooling; but as nearly all of the crystals show the effects of abrading action, it is often difficult to distinguish planes confined within such narrow limits, and which are too small or too rough to admit of accurate measurement. Indeed, the faces of the crystals are in most instances slightly rounded, even in specimens obtained directly from veins, and which, consequently, cannot have been exposed to attrition.

Gold may sometimes be obtained in crystals by cooling, but when these are formed it is more by accident than design, for it is impossible to regulate the rate of cooling. Recently, during the preparation of a plate of fine gold in the Royal Mint, some splendid specimens of pure gold crystals were incidentally obtained by W. Chandler Roberts.

Composition of Native Gold.—Native gold is never quite pure, being almost invariably alloyed with silver, and containing frequently small proportions of copper and iron. In Siberia it is often associated with platinum, and in the Gongo Soco mines in Brazil an alloy of gold and palladium of a pale yellow colour is sometimes found. In Columbia a somewhat similar mixture is procured, in which the palladium is replaced by another rare metal, rhodium. In Hungary it is met with in combination with tellurium and other elements. The specific gravity of native gold varies from 13·3 to 18·5.

The proportion of silver, the principal ingredient which is found in combination with gold, varies from 1 to 50 per cent.; and not only differs greatly in specimens of native gold obtained from diverse regions, but even to a certain extent in specimens from the same auriferous district. In general, however, the composition of the gold of the same district is remarkably constant; so much so, that the knowledge of the locality whence it is derived is often sufficient to enable the experienced assayer to guess pretty nearly the quantity of pure gold which the compound contains. The subjoined table (see next page) presents the composition of native gold from various parts of the world.

The Australian gold, it will be observed, is notably richer than that from any of the other great divisions of the globe. For additional analyses of native gold the reader may be referred to Gmelin's "Handbook of Chemistry" (the Cavendish Society's translation), vol. vi. pp. 247–250, where over sixty will be found.

Preparation of Pure Gold.—The methods adopted for obtaining *commercially* pure gold on a large scale will be given when considering the metallurgical treatment of gold ores; but it may be well in this place to describe the modes usually adopted in the laboratory with a view to obtain *chemically* pure gold.

Very many substances have the property of depositing gold in the metallic state from its solution in nitro-hydrochloric acid, and this fact is taken advantage of for the purpose now under consideration. Chemists have differed as to the best reducing agent for the terchloride of gold, that usually recommended being the protosulphate of iron. Levol, however, prefers the protochloride of antimony, and others again oxalic acid, or a stream of sulphurous acid gas.

At the latter end of 1873 a large quantity of absolutely pure gold (about 75 ozs.) was required for use as a standard, with which the composition of the British gold coinage might be compared. The preparation of this plate was intrusted to the chemist of the mint, and with a view to obtaining the purest gold possible numerous experiments were made. The method finally adopted consisted in the precipitation of gold by means of oxalic acid, and as this plate was purer than that given by other means, it may be as well to describe at some length the precautions which were observed in its preparation.

A hundred ounces of gold, selected for its purity, were dissolved in nitro-hydrochloric acid. The greater part of the chloride of silver derived from the silver which the gold contained was removed by allowing it to settle, and decanting the clear supernatant liquid, and this was evaporated to dryness with the addition of hydrochloric acid. After careful testing for the metals of the platinum series by means of chloride of potassium and alcohol, the mass of chloride of gold was dissolved in distilled water, and after diluting to over 100 gallons, was allowed to stand in glass vessels for fourteen days. The dissolved chloride of silver was deposited from the solution upon the sides of the vessels, from which the liquid was then removed into other glass receptacles, the precipitation of the metallic gold from this solution being effected by means of oxalic acid. The resulting metal was boiled repeatedly with hydrochloric acid and distilled water, then dried, melted, and cast into a stone mould.

Composition of Native Gold from Various Parts of the World.

Locality.	Authority.	Gold.	Silver.	Iron.	Copper.
Europe.					
Great Britain—					
Vigra and Clogau,	Claudet.	88·5	5·0	—	—
" "	Forbes.	90·16	9·26	trace.	trace.
" "	"	89·83	9·24	trace.	none.
River dust (Mawddach),	*Phil. Mag.*, Nov. 1867.	84·89	13·99	·34	trace.
Wicklow (River),	Mallet, *Phil. Mag.*	92·32	6·17	·78	—
Welch Gold Mining Co.,	Claudet.	76·4	22·7	—	—
Transylvania,	G. Rose.	60·49	38·74	—	0·77
"	"	84·89	14·68	·13	·04
"	Fremy et Pelouze.	64·77	35·23	—	—
Asia.					
Russian Empire—					
Berezovsk,	G. Rose.	91·88	8·03	trace.	·09
Ekaterinburg,	"	98·96	·16	·05	·35
Gozuschka or Boruschkoi,	"	83·85	16·15	trace.	trace.
Siberia,	Fremy et Pelouze.	86·50	13·20	0·30	
Petropawlowsk (washings),	G. Rose.	86·81	13·19	trace.	trace.
Miask (washings),	"	89·35	10·65	trace.	trace.
Berezovsk (in brown Hematite),	"	93·78	5·94	0·04	0·08
Africa.					
Anamaboc,	T. H. Henry.	98·06	1·39	0·15	
"	"	88·25	11·17	·36	·10
America.					
South—					
New Granada,	Boussingault.	64·93	35·07	—	—
Marmato,	"	73·45	26·48	—	—
North of Brazil,	Rivot.	91·0	8·7	—	·03
Brazil,	D'Arcet.	94·0	5·85	—	—
" (North),	Rivot.	91·0	8·7	0·3	—
"	Levol.	91·0	8·7	0·3	—
" (Gongo Soco mines)	T. H. Henry.	83·36	6·44	—	0·50Cu, 3·58Pd
Ogas Anchas,	Boussingault.	84·5	15·5	—	—
Santa Rosa de Osos,	"	82·4	15·5	—	—
Central America,	Fremy et Pelouze.	88·04	11·96	—	—
North—					
California,	T. H. Henry.	90·12	9·01	—	0·87
"	"	86·57	12·33	0·24	0·29
"	Rivot.	89·10	10·50	0·20	—
"	"	90·90	8·70	0·20	—
"	"	93·00	6·70	—	—
"	Makins.	88·70	10·70	0·66	
"	Levol.	92·70	6·90	—	0·40
"	—	90·70	8·80	0·38	
Mariposa (quartz gold),	F. Claudet.	81·00	18·70	—	—
Georgia,	W. W. Mather.	95·58	4·42	trace.	trace.
Canada,	T. H. Henry.	90·38	9·53	—	—
" (Rivière du Loup),	T. S. Hunt.	86·40	13·60	—	—
British Columbia—					
Cariboo,	Claudet.	84·25	14·90	—	—
"	T. L. Phipson.	93·75	6·25	—	—
Titiribi,	Rose.	76·41	23·12	—	0·03
Stephen's Creek,	Claudet.	79·50	19·70	—	—
Locality not given,	"	86·10	13·50	—	—
Vancouver's Island,	F. Wibel.	91·86	6·63	0·51	1·0
Australia—					
South Australia,	A. S. Thomas.	87·78	6·07	6·15	—
Bathurst,	T. H. Henry.	95·69	3·92	0·16	—
Ballarat,	Claudet.	99·25	0·65	—	—
Australia,	Makins.	98·20	1·0	—	—
"	"	95·33	4·03	0·60	
"	"	95·04	3·76	—	—
"	"	94·64	4·95	0·41	
"	Fremy et Pelouze.	99·28	0·44	0·28	
New Zealand—					
Not known,	Claudet.	96·25	3·55	—	—

The ordinary method, adopted when such absolute purity is not essential, consists in dissolving a quantity of gold (the purest that can be conveniently obtained) in nitro-hydrochloric acid, formed by adding 1 part of nitric acid, of specific gravity 1·33, to 2 parts of commercial hydrochloric acid. This will give a solution of terchloride of gold, mixed with chloride of silver if any of that metal be present. The solution thus obtained is evaporated with an excess of hydrochloric acid for the purpose of destroying the excess of nitric acid. The residue is then treated with hot water, by which it is dissolved, with the exception of the chloride of silver, from which the solution is decanted or separated by filtration.

An excess of protosulphate of iron in solution is then added to the auriferous solution in the proportion of 4 or 5 parts of the crystallized protosulphate (green vitriol) to 1 of gold; and the mixture is put in a warm place, and allowed to stand for several hours. In the reaction which occurs, the chlorine that was combined with the gold unites with a portion of the iron of the protosulphate, part of which is thereby converted into sesquisulphate, while sesquichloride of iron is at the same time formed, and metallic gold is precipitated. This reaction is represented in the annexed equation:—

$$6FeSO_4 + 2AuCl_3 = 2(Fe_2 3SO_4) + Fe_2Cl_6 + 2Au.$$

In place of the iron salt, LEVOL prefers to add an excess of the protochloride of antimony, dissolved in dilute hydrochloric acid, in which case the following equation exhibits the reaction that takes place:—

$$3SbCl_3 + 2AuCl_3 = 3SbCl_5 + 2Au.$$

In this case if chloride of silver be present, it is retained by the hydrochloric acid in solution. The gold is deposited after the lapse of a few hours in the form of a finely-divided powder, which when suspended in water is brown by reflected and purple when viewed by transmitted light; but under the burnisher it readily assumes the metallic lustre and characteristic colour of gold. It also admits of being aggregated and welded together by percussion; and if heated to whiteness, and in that state struck repeatedly with a heavy hammer, its particles become united into a solid mass, without having being raised to the point of fusion.

To obtain the gold in a perfectly pure state, however, the precipitated powder is boiled with hydrochloric acid of specific gravity 1·1, which is then decanted, and the residue is boiled twice with fresh acid. The gold is *not* washed between these successive treatments with acid, which remove the last traces of iron, and nearly all the chloride of silver.

Lastly, the gold is well washed, dried, and mixed with its own weight of bisulphate of potassa, or a small quantity of borax and nitre, and fused in a Hessian crucible exposed to a very strong heat. By this operation the last portions of chloride of silver are removed, and a button of perfectly pure gold is obtained.

Properties of Pure Gold.—Pure gold is of a rich slightly reddish-yellow colour, and possesses high metallic lustre, taking a brilliant polish. When hammered into leaves it appears green by transmitted and red by reflected light; the colours in the two cases being, of course, complementary, and they would, if combined, produce white light. When finely subdivided it possesses a brown or purple colour. Gold crystallizes in quadrangular pyramids and octahedra, and in forms derivable from the cube, many of which have been already referred to. Its specific gravity, when fused, is generally given as about 19·2, and it varies to 20·72, according to its state of aggregation and the method by which it was prepared. Experiments were recently made in the Royal Mint to determine the specific gravity of a large casting of absolutely pure gold, weighing about 75 ozs. (Troy), firstly, before rolling, and secondly, after once passing through the rollers, when the specific gravity was found to be slightly increased, as the following figures show:—

Specific gravity before rolling	19·2945
" " after once rolling	19·2982

The following table of specific gravities of gold in various conditions may be of interest:—

Condition in which the Gold Exists.	Specific Gravity.
Fused gold	19·2
Hammered gold	19·3 to 19·4
Gold after fusion, *per se*	19 3 to 19·4
" " under carbonate of soda	19·32 to 19·33
" " under borax	19·33 to 19·34
" " under common salt	19·30
" pressure under die	19·31 to 19·34
Large mass (70 oz.) pure gold cast in plate	19·2945
The same after once passing through the rolling mill	19·2982
Finely divided gold deposited by protosulphate of iron	19·55 to 20·72
Finely divided gold deposited by oxalic acid	19·49

Its equivalent is usually given as 197, but the most accurate value of it appears to be that given by Dr. WATTS, namely, 196·71. As already mentioned, pure gold is nearly as soft as lead, but it materially differs from that metal in its malleability and ductility, in which it exceeds all metals. It may be hammered into leaves of about the 300,000th of an inch in thickness, and a single grain may be extended over 56·75 square inches of surface, or drawn out into a wire 500 feet long. RÉAUMUR, by rolling out a fine gilt silver wire, reduced the coating of gold to the 12,000,000th of an inch in thickness, and the surface appeared to be perfect when viewed under the microscope. FARADAY found that ordinary gold leaf may be considerably reduced in thickness without destroying it, by floating on a dilute solution of cyanide of potassium. If such a film be attached to a sheet of glass the reflected light is yellow, and transmitted, as usual, green; but if this be now exposed to a temperature not exceeding 600° Fahr. for some time, the metallic lustre disappears, and transmitted light becomes ruby-red.

In tenacity gold is inferior to iron, copper, silver, and platinum.

Gold does not combine directly with oxygen, and therefore suffers no change by exposure to air and

moisture at any temperature—not even by being kept in a state of fusion in open vessels. It is not attacked by the mineral or any of the simple acids, except selenic, and then only by the aid of heat.

The alkalies have no action on gold, but when heated with it in contact with air an absorption of oxygen takes place, with the formation of an alkaline aurate. Nitre, in a state of fusion, attacks it. The persulphides, either in the wet or dry state, also attack it, with the formation of sulphide of gold. Iodine has only a weak action upon it, but bromine and chlorine attack it easily at ordinary temperatures; and it is dissolved by any substance which liberates chlorine. It is therefore dissolved by hydrochloric acid, if binoxide of manganese or chromic acid be added thereto. Its usual solvent is that already mentioned—a mixture of 1 part of nitric acid and 2 parts of hydrochloric acid. *Nascent chlorine*, which is eliminated by the mutual action of the mixed acids, dissolves gold; the gas forming with the metal a terchloride, which is readily soluble in water. The conducting powers of pure gold for heat and electricity are rather more than half those of silver, for if in each case the conductivity of this latter metal be taken as 100 we have for gold—

Conductivity for heat,	53·2
Conductivity for electricity at 72° F. (21·8° C.),	55·19

As will be seen from the commencement of this article the melting point varies, according to different observers, from 2192° Fahr. (1200° C.) to 2596° Fahr. (1424° C.). Dr. Riemsdijk, after a comparison of the results of various observers, concluded that 2264° Fahr. (1240° C.) was most probably correct, a temperature nearly identical with that given by Pouillet. It is therefore less fusible than silver, the melting point of which is 1873° Fahr. (1040° C.), and more so than copper, which melts at 2426° Fahr. (1330° C.).

In fusion it exhibits a bluish-green colour. It is not sensibly volatile in the strongest heat of a blast furnace; but in the focus of a large convex lens, in the intense heat of the oxyhydrogen jet, or under the influence of a powerful electric discharge, a gold wire is dispersed in vapour; and if, in the latter case, the wire be placed just above the surface of a sheet of paper, the course of the discharge is marked by a broad, dark, purple stain, produced by the finely-divided gold. If, instead of the sheet of white paper, a plate of polished silver be employed, it is traversed by a brightly-gilded line, which is firmly attached to its surface. When a globule of gold is placed between the terminal charcoal points of a powerful voltaic battery, it enters almost immediately into fusion, and gives off abundant metallic fumes.

Gold contracts on cooling, and cannot be advantageously employed for castings, as it shrinks greatly at the moment of solidifying.

It has been shown that native gold affords numerous well-defined crystals belonging to the cubic system, and that of these the greater number, if not all, are affected by the faces of the regular octahedron.

According to Knaffl, gold in a crystalline state may be obtained by treating its amalgam in the following manner:—1 part of finely divided gold as precipitated from solution is formed into an amalgam with 20 parts of mercury, and after the whole has been maintained during eight days at a temperature of 80° C., nitric acid of specific gravity 1·35, also at this temperature, is added. The gold is thus left in a crystalline form, retaining, however, traces of mercury, but after this has been expelled by the aid of a gentle heat, the crystals assume a brilliant appearance.

Chemical Examination of Gold Ores.—A rude method of ascertaining the presence of gold in crushed quartz, or earthy ore, by washing with the hand-basin, has been described; but gold is often present in the matrix in grains or particles so minute that it cannot be detected by the eye, and sometimes it is quite disguised by admixture with other metals or minerals.

In these cases it is necessary to resort to a chemical examination, that previously described being exclusively mechanical. In commencing mining operations, the first point to be determined is, of course, whether gold exists in any appreciable quantities; and if this be decided in the affirmative, the next point is to determine the *proportion or quantity of gold* contained. The first process is termed *testing for gold*, or the *qualitative examination* of a suspected mineral; the second is the *quantitative examination*, or *assaying* process.

Sulphate of iron, protochloride of tin, and oxalic acid are the tests or reagents pre-eminently employed in seeking to determine the presence of gold.

Before any of these tests can be applied, the substance supposed to contain the gold must be brought into a state of solution; and this can only be done by means of the mixture of nitric and hydrochloric acids already mentioned. If the substance consist of earthy or quartzose matter, this must be reduced to powder by trituration in a mortar before it is subjected to the action of the solvent; but if the matter under examination be simply a metallic alloy, it can be dissolved without any previous preparation, and an excess of acid should be avoided. When the solution is effected, the liquid should be evaporated to about one-eighth of its original bulk, and then diluted with 3 or 4 ozs. of water. The action of the reagents is as follows:—

1. *Sulphate of Iron or Green Vitriol.*—If a few crystals of this salt be dissolved in distilled water, and dropped into the suspected solution, the result is the precipitation of the gold, if any be present, in the form of a dark-brown powder, which is metallic gold in a very fine state of division, as already described in connection with the laboratory process for preparing pure gold. If the solution has been mixed with a considerable quantity of water, the liquid, on the addition of the green vitriol, is coloured brown by reflected, and blue or a dingy green by transmitted light; and this is obvious even when 40,000 parts of the solution contain only 1 part of gold. If the liquid amount to 80,000 parts, it is coloured sky-blue; with 160,000 parts, it becomes violet; with 320,000 parts of liquid, the violet tint is still

very obvious; but with 640,000 parts it is with difficulty perceived.

The deposit formed when the sulphate of iron is added may be corroboratively proved to be gold, by its being insoluble in nitric acid, but readily soluble in aqua regia.

2. *Protochloride of Tin.*—If to another portion of the nitro-hydrochloric solution be added a small quantity of a solution of protochloride of tin (commonly known as *salts of tin*), there will be immediately produced, if any gold is present, a dark brownish-purple precipitate, known as *purple of Cassius*. This substance is used in enamel and porcelain painting, and also for tinging glass of a fine red colour, in connection with which applications it will be noticed afterwards. Its colour, though not a brilliant purple, but rather a reddish-brown, is characteristic, and after being once seen is not likely to be mistaken. Its appearance, when the chloride of tin is added to the liquid, affords an infallible proof of the presence of gold, for a very minute portion of that metal gives a manifest reaction when this test is employed.

When the first test (sulphate of iron) has been applied, and its evidence corroborated by the solution of the precipitated gold powder in aqua regia, the protochloride of tin may be employed to produce the purple of Cassius in this solution also.

3. *Oxalic Acid.*—This substance, either in crystals or dissolved in water, causes when added to the solution of gold the precipitation of any of that metal in a form which varies with the temperature and strength of the solution. The action takes place very slowly in the cold, but immediately on applying heat there is a copious evolution of carbonic acid gas, hydrochloric acid being also formed during the process.

This reaction has been more completely described in the account of the preparation of pure gold. A crystal of oxalic acid, wetted with a solution of gold, becomes soon covered with a thin film of the metal.

These are the tests most easily applied by persons unaccustomed to chemical manipulation. Gold, however, gives characteristic reactions with several other reagents, which it is convenient to give in a tabular form.

TESTS FOR GOLD.

Test or Reagent.	Result.
Sulphate of protoxide of iron,	In very dilute solutions, only a blue coloration; in stronger acid solution the gold is deposited as an orange-brown powder.
Protochloride of tin,	Brown or purple-red precipitate or coloration, varying with the strength of solution.
Oxalic acid,	Black or golden coloured precipitate or coloration, dependent upon temperature and strength of solution.
Potash,	Produces no precipitate when in excess, unless containing organic matter, in which case aurous oxide is deposited. After some time, potash alone produces a green coloration and slight precipitate.
Ammonia,	Yellow precipitate of fulminating gold.
Carbonate of Potash,	No precipitate in cold solutions, but voluminous one like oxide of iron when heated.
Carbonate of ammonia,	A yellow precipitate of fulminating gold, with evolution of carbonic acid.
Ferrocyanide of potassium,	Emerald green coloration.
Cyanide of potassium,	Yellow precipitate soluble in excess.
Protonitrate of mercury,	Black precipitate.
Protochloride of antimony,	Brilliant yellow precipitate of metallic gold.
Iodide of potassium,	Colours liquid black, and then throws down a greenish-yellow precipitate of auric iodide.
Tannic acid,	If added to solution containing gold and potash in excess, produces a deep black precipitate of protoxide of gold.
Sulphate of ammonium,	Precipitates a blackish-brown tersulphide of gold, soluble in an excess of the reagent, provided the latter contains an excess of sulphur.
Sulphuretted hydrogen,	Black precipitate, even in very acid solutions.
Hypophosphorous, phosphorous, or sulphurous acid,	Reduces gold to metallic state. When the solution is weak it becomes blue, depositing gold on being boiled.
Metallic zinc,	Deposits gold as a brown precipitate.

In addition to the above, a great number of organic substances deposit gold from its solution in aqua regia, especially in presence of an excess of potash.

The above reactions are so characteristic that it is impossible to mistake gold for any other metal, the protochloride of tin test being capable of detecting (by a faint coloration) the presence of 1 part of gold in 640,000 of the liquid under examination. The protochloride solution should also contain a little bichloride of tin—a mixture most conveniently produced by adding a little chlorine water to the solution of the protochloride.

Tests for Metals usually Associated with Gold.—In examining an ore or alloy supposed to contain gold, it is often an object of great importance to determine the nature of the metals with which the gold is associated. These may be of high value on their own account, and, according to the quantities in which they are present, may greatly affect the value of the ore or mineral in question. To enter fully into the subject in connection with the rarer metals that are found associated with gold would be of little practical use. Attention should, however, be specially directed to the means of detecting and distinguishing those of most common occurrence—namely, copper, silver, and platinum.

1. *Copper.*—It has been shown that copper is almost always associated with gold even in quartz, and that copper pyrites is one of those substances frequently mistaken for gold. When dissolved in acids, however, it gives characteristic reactions, which render its presence easily distinguishable. One of the readiest tests is to introduce into the solution a piece of clean iron, when, if copper be present, it will be

deposited on the iron in the metallic state, an effect which is due to a simple exchange of place between the metals, the iron passing into solution while the copper exhibits itself in the solid form.

Again, when ammonia is added in excess to a solution in which copper exists, it communicates to the liquid a rich deep blue colour. Ferrocyanide of potassium produces, with copper, a brownish-red precipitate, even when the metal is present in very small quantity. Carbonate of soda precipitates copper from its hot solutions in the form of an apple-green compound, which is a carbonate of copper, known, when artificially formed, as *verditer*, and when it occurs native, as *malachite*. Copper ore in the latter form exists abundantly in Australia—not, indeed, mixed with the gold, but constituting valuable mines, from which the ore is sent over to this country to be smelted in South Wales.

The above are the principal and most common tests for copper, and generally suffice for the detection of its presence. It may, however, be well to give in a tabular form its reactions.

TESTS FOR COPPER.

Test or Reagent.	Result.
Potash or soda,	A light blue bulky precipitate insoluble in excess. With strong solution and excess of precipitant, the precipitate after lapse of time turns black. In any case it becomes black on boiling.
Carbonate of potash or soda,	Blue precipitate, becoming black on boiling.
Ammonia or carbonate of ammonia,	Greenish blue precipitate soluble in excess of reagent, forming blue coloured fluid. A precipitate of blue hydrated oxide of copper is produced by adding an excess of potash, slowly in the cold, but immediately on heating.
Hydrosulphuric acid or sulphide of ammonia,	Black precipitate of sulphide of copper, insoluble in ammonia.
Ferrocyanide of potassium	In moderately dilute solutions a red-brown precipitate, if very dilute only a coloration. This precipitate is decomposed by potash.
Ferridcyanide of potassium,	Yellowish green precipitate.
Oxalic acid,	Clear greenish-blue precipitate.
Iodide of potassium,	White precipitate.
Tannin	Grey precipitate.
Chromate of Potassium,	Reddish-brown precipitate.
Iron,	Introduced into solutions of copper salts is covered with coating of metallic copper. Reaction assisted by presence of free acid.
Zinc,	If introduced together with copper salt solution, even very dilute, and free hydrochloric into platinum dish, this latter is coated with surface of copper.

If a platinum wire be dipped in a copper salt solution containing free hydrochloric acid, and then held in the flame of a Bunsen's burner, the flame will show an emerald green tint. This test is applicable to the detection of exceedingly minute quantities.

2. *Silver.*—It has been shown that gold is invariably alloyed with this metal, sometimes to a very large amount. In its separate state it is readily distinguished, not only by its white colour, but also by its specific gravity, which is only 10·4, or about one-half that of gold. It may be useful to state, that when in a very fine state of division it is of a dark-grey colour. It may be easily recognised by its chemical behaviour with reagents, in which respect it differs from gold by its solubility in nitric acid at all temperatures, and in hot sulphuric acid. On the contrary, with hydrochloric acid it forms a white curdy precipitate, which is the chloride of silver. If the nitric acid employed to dissolve it contain the least hydrochloric acid, the solution will become turbid by the formation of the chloride. Hence, when a mineral containing gold and silver is submitted to the action of aqua regia (nitro-hydrochloric acid), the appearance of this white precipitate will immediately indicate the presence of the latter metal. The chloride of silver is soluble in ammonia, and may thus be distinguished from many other white precipitates; or it may be further tested by putting the precipitate into a crucible with carbonate of soda, and exposing the mixture to a strong red heat, when a button of pure silver will be obtained. By careful manipulation the amount of silver present may be accurately determined in this manner. If the mineral containing the silver be dissolved in oil of vitriol, the metal is readily detected by inserting a few fragments of copper, which cause the precipitation of the silver in a pulverulent state.

A table is given below for silver similar to those which precede for gold and copper; and as gold never occurs without being associated to a greater or less extent with silver, it may be useful to compare the effects of identical reagents in the two cases:—

TESTS FOR SILVER.

Test or Reagent.	Result.
Sulphate of protoxide of iron,	In neutral solutions, a white precipitate of metallic silver.
Protochloride of tin,	White precipitate of chloride of silver, which is changed into metallic silver on the addition of an excess of the reagent.
Oxalic acid,	White precipitate soluble in ammonia.
Potash,	Clear brown precipitate turning black on boiling; insoluble in an excess of the reagent, but soluble in ammonia.
Ammonia,	If added in small quantities, produces a brown precipitate soluble in excess of the reagent. The solution requires to be neutral or alkaline.
Carbonate of soda or potash,	White precipitate soluble in ammonia.
Carbonate of ammonia,	White precipitate soluble in excess.
Ferrocyanide of potassium,	White precipitate.
Ferridcyanide of potassium,	Reddish-brown precipitate.
Iodide of potassium,	White or slightly yellow precipitate slightly soluble in an excess of the reagent.

Chromate of potassium,	Reddish-brown precipitate slightly soluble in water, very soluble in ammonia.
Sulphide of ammonium, or sulphuretted hydrogen,	Black precipitate, which is decomposed and dissolved by boiling nitric acid with separation of sulphur.
Phosphate of soda,	Yellow precipitate; the liquid becoming acid.
Pyrophosphate of soda,	White precipitate; the liquid remaining neutral.
Hydrochloric acid, or soluble metallic chlorides,	White curdy precipitate of chloride of silver; in very dilute solutions at first, only a bluish-white coloration, but chloride separates after standing in a warm place. Turns first violet, then black, on exposure to light. Very soluble in ammonia.
Metallic zinc or copper,	Precipitate of white metallic silver.

The presence of a trace of the protochloride of mercury prevents the chloride of silver from changing its colour under the influence of light.

3. *Platinum.*—This is another metal frequently associated with gold; and as it is one of the noble metals, and ranks in price between silver and gold, an ore which contains it in any quantity is of considerable value. The specific gravity of platinum varies from 21·47 to 21·53; according to Deville and Debray, however, it is only 21·15. It will thus be seen to be higher than that of gold; indeed platinum, osmium, and iridium are the heaviest of all known metals, all three possessing about the same specific gravity: possibly osmium is slightly heavier than the other two. Platinum is of a light steel-grey colour, less ductile than gold or silver, but more tenacious, indeed it will support greater weights on equal thicknesses of wire than any metal except iron or copper. It is distinguished from gold not only by its colour, but also by its extreme difficulty of fusion; it does not melt by itself in the highest heat of a furnace, but softens sufficiently to admit of forging and welding, and in the arc of flame of the voltaic current, or before the oxyhydrogen blowpipe, it admits of being fused even in considerable masses. On the other hand, it resembles gold not only in its high specific gravity, as already stated, but also in the fact that it resists the action of all the simple acids, and is soluble only in aqua regia. This circumstance, together with its great infusibility, renders it of important use in many of the arts, and indispensable for various purposes in the laboratory. It is the metal universally employed for apparatus which requires to be exposed to high temperature and powerful chemical agencies, without undergoing any change. It is therefore very important that miners in the gold-fields should look carefully for this metal, which, being destitute of any glittering appearance, is likely to escape the notice of an ordinary observer.

There are, however, certain chemical reactions by which platinum may be readily distinguished and separated from gold in a solution. Sulphate of iron and oxalic acid, which precipitate gold, do not precipitate platinum. When the latter is dissolved in aqua regia, and the acid neutralized by carbonate of soda, the metal is deposited as a black powder, if the mixture be boiled with tartaric acid and soda. Further, the addition of chloride of ammonium and alcohol to a strong solution of platinum causes the deposition of a yellow crystalline precipitate, which is characteristic of this metal. These and other reactions may be summarily stated as follows:—

TESTS FOR PLATINUM.

Test or Reagent.	Result.
Sulphate of protoxide of iron.	No precipitate.
Protochloride of tin,	Produces in solutions containing excess of hydrochloric acid an intense brown-red coloration, but no precipitate.
Oxalic acid,	No precipitate.
Potash,	Yellow precipitate soluble in an excess of reagent with application of heat.
Ammonia,	Yellow precipitate soluble in great quantity of water or in an excess of ammonia.
Carbonate of potash, or carbonate of ammonia,	Yellow precipitate, especially in solution of bichloride of platinum.
Ferrocyanide of potassium,	No precipitate, but yellowish green coloration.
Ferridcyanide of potassium,	Same reaction.
Protonitrate of mercury,	Reddish-yellow precipitate.
Iodide of potassium,	Brown coloration at first, afterwards a yellow precipitate.
Sulphide of ammonium,	Black precipitate soluble in a great excess of the reagent, provided this contains free sulphur.
Sulphuretted hydrogen,	Blackish-brown precipitate after a time or at once on heating.
Metallic zinc.	Black precipitate of metallic platinum after a time.

The above tests are specially applicable to the solution of bichloride of platinum, such as is obtained by dissolving platinum in nitro-hydrochloric acid.

Application of the Reagents.—Having thus described the properties and characteristic reactions of the different metals which it is desirable to look for as being frequently associated with gold, let it now be assumed that the substance to be examined is a piece of auriferous quartz. This must be first reduced to powder, and then boiled for some time in an earthenware or glass dish with aqua regia. The solution is then diluted with water, passed through a filter, and allowed to cool. If any silver be present, it will remain in the filter as a white precipitate, mixed with the quartz.

To the liquid which has passed through the filter, a solution of carbonate of soda is now added, until no more effervescence takes place. This will precipitate all the other metals which may be present except gold and platinum, which will remain in solution.

The liquid is again filtered, and a solution of oxalic acid is added until it ceases to produce effervescence, and has a sour taste; then boil; if there be any gold present it will be precipitated as a dark powder. The platinum, if any be present, will still remain in solution.

Decant or filter the liquid from the gold precipitate, and add to the former protochloride of tin, when a reddish-brown colouring will appear if platinum be

present. Or, by boiling with tartaric acid and soda, the platinum will be thrown down as a black precipitate.

It has been stated that if any silver be present, it will be found on the first filter, mixed with the quartz. Wash this with ammonia, which, if copper be present, will produce a deep blue tinge. To the solution which comes through, add hydrochloric acid until the smell of ammonia disappears, and the silver will be thrown down as a white curdy precipitate.

It is evident that other methods and reagents may be adopted. For example, the original solution in aqua regia may be concentrated by evaporation, until it is very much reduced in quantity; then add about three-fourths of its bulk of spirits of wine, and lastly, a saturated solution of chloride of ammonium. By these reagents the platinum will be thrown down as a yellow crystalline precipitate, while the solution filtered from this, and treated with sulphate of iron or boiled with oxalic acid, deposits gold.

By carefully weighing the gold obtained, the amount present in a given quantity of the ore or alloy may be exactly determined; but full details of the different methods of conducting the quantitative examination, including the assaying of gold ores and alloys by the dry process, will, to avoid repetition, be postponed to the close of the article.

Mechanical Preparation of Gold Ores.—Before subjecting the ore, or the auriferous gangue, to the chemical or metallurgical processes by which the gold is extracted, it has certain mechanical operations to undergo, the number and nature of which will be determined by the character of the ore itself, and its state of aggregation. The metal is rarely found in the shape of large nuggets, requiring only to be cast into ingots. It is generally either in the shape of dust or spangles, or small grains intimately mixed with the quartz rock or the alluvial soil; and though the greatest amount of gold is obtained by the direct washing of alluvial deposits, yet, as a considerable proportion is extracted from the solid rock, it seems to be the natural order to begin with those operations by which the rock is artificially reduced to the state of an auriferous sand or pulverized ore. These mechanical operations are, in California, usually two in number, namely (1), rough crushing in ore-breakers, and (2) stamping in the stamp-mill, in which apparatus a partial amalgamation of the freed gold also takes place.

Crushing.—The apparatus formerly employed for reducing the ore to a size suitable for introduction to the stamping mill consisted of two powerful cast-iron rollers, whose axes were in the same horizontal plane, and were arranged in a solid iron frame so that their distance apart was variable. The ore being placed above the space between these rollers was, by their revolution, drawn in and crushed; one roller being so held in position by a lever and weight as to yield when it experienced any extra pressure due to an excessive hardness of the ore. This apparatus has since 1861 been almost universally replaced by an instrument known as "Blake's Rock Breaker," which is shown in section in Fig. 13 as employed in California, that manufactured in Europe differing slightly in construction.

It consists essentially of a strong iron frame, supporting upright convergent iron jaws, usually faced with hard white iron, one of which jaws, K, is fixed (bedded in zinc), and the other, M, movable, being actuated by a revolving shaft. Stones or masses of rock are dropped into the space, L, between the jaws; and a reciprocating or vibratory motion given to M, causes them to drop lower in the wedge-shaped space till sufficiently broken to drop out at the bottom, this opening being variable in order to adjust the fragments to any size required. The action is as follows:—The dotted circle, D, shows the position of the engine shaft, E being the crank connected with it. This

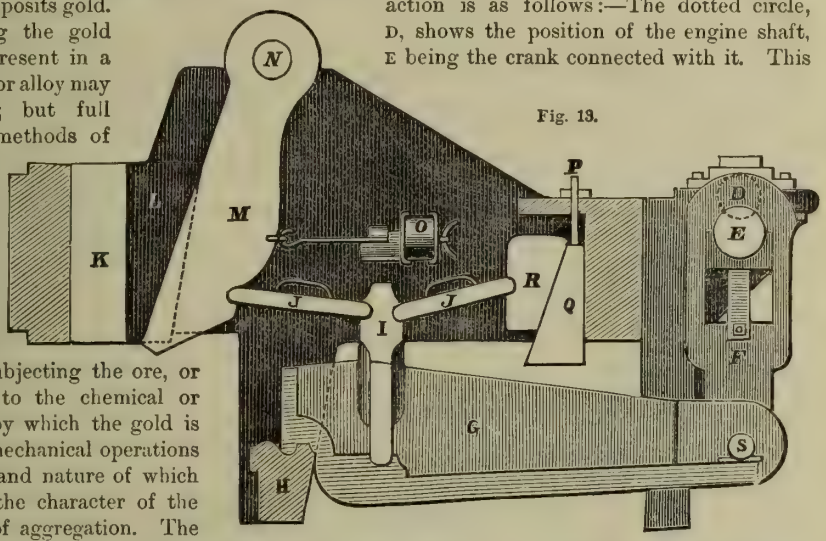


Fig. 13.

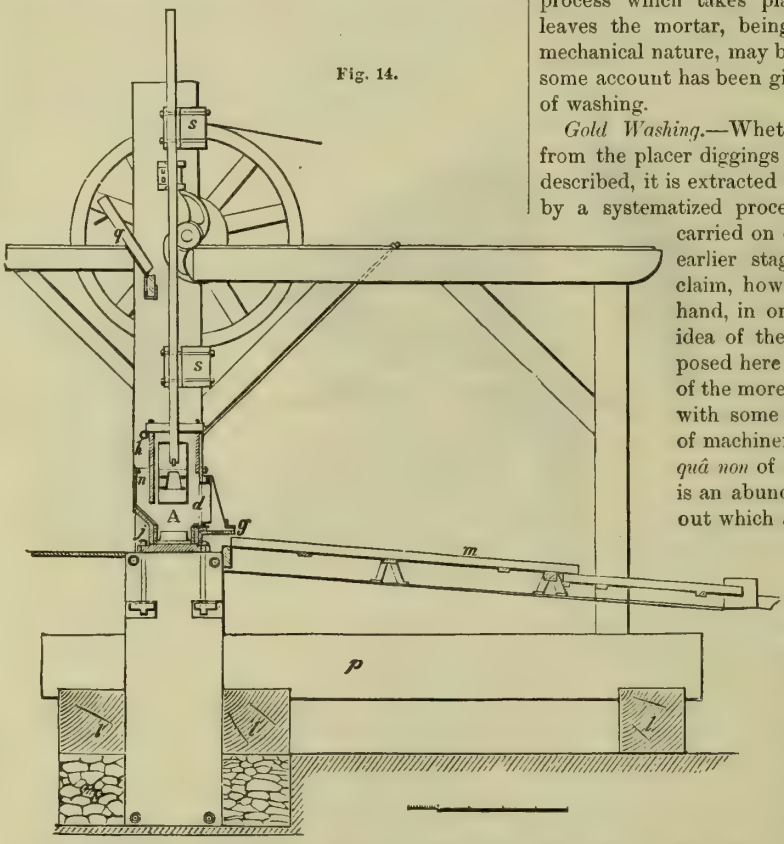
crank is connected by means of a connecting-rod, F, with a heavy lever, G, having its fulcrum at H; and from G rises a vertical piece, I, against the top of which "toggles," J J, have bearings. The movable jaw, M, being pivoted at N, is pressed towards K during an upward motion of the crank, E, and when this descends is drawn back by an india-rubber spring, O. The wedge-shaped piece of metal actuated by the screw, P, is employed to adjust the opening at the lowest point of M. It is said that by means of this machine the hardest rock can be broken with great facility, the amount broken varying from 4 to 6 cubic yards per hour, according to the size of machine and of the fragments produced.

An improved patent "Blake's Rock Breaker" has been recently introduced by Marsden, which is capable of breaking from 100 to 120 tons of lime-stone per hour, at a cost of ·15 dollar per ton.

Stamp Mill.—The quartz, after being broken by the rock breaker into pieces of about the size of a walnut, is discharged upon a platform immediately in front of the battery of the stamp mill, the

general arrangement of which is represented in Figs. 14 and 15, the former representing a front and the latter a side elevation. It consists essentially of an iron mortar, A, fixed on a solid wooden block, *a*, this latter resting firmly on the bed-rock. Inside the mortar works the stamp, weighing from 600 to 900 lbs., and attached to a wrought-iron stem, which works in guides, *s*, *s*. On this stem is fixed a tappet, which is acted on by a cam on a horizontal shaft, to which motion may be given by either steam or water power. It will be seen that by this means the stamp is elevated by the rotation of the cam, and after attaining a certain elevation (usually about 10 inches), is suddenly dropped, thus crushing the ore placed underneath it. The friction between

Fig. 14.



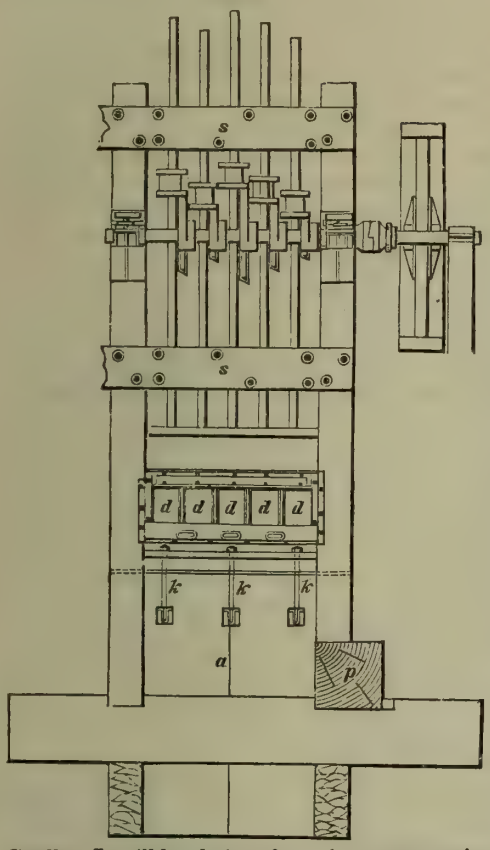
the cam and tappet causes the stamp to rotate, thus insuring an even wear of the latter, which is shod with a piece of white iron slowly cooled, and strikes a similar die, placed on the bed of the mortar, A. A battery usually consists of four or more mortars placed side by side, as shown in the figure, the cams being so arranged that no two stamps are set free at the same time. At the back of the mortar at *d* is fixed a screen, through which the pulverized ore passes, it being provided with fine round holes or longitudinal slits, three-eighths of an inch long and ·02 inch wide, which are in horizontal rows about ·04 inch apart. It is essential that the ore should be thus fine, in order to free the particles of gold from surrounding matter, as otherwise the mercury would be unable to form an amalgam. From this screen the ore is delivered direct to the sluices, to be presently described. While the battery is in action, water is introduced by means of a pipe at the top of the mortars, and the battery is supplied with ore by hand, the supply being so regulated that there shall not be more than 2 inches of sand between the die and the shoe at the end of a drop. The number of these drops varies with the weight of the stamp, being usually about 60 a minute. A 20-stamp battery would crush from 30 to 40 tons of an average quartz rock in twenty-four hours. The quantity of water required is about a half cubic foot per stamp per minute, but it varies with the nature of the ore. The description of the amalgamation process which takes place after the crushed ore leaves the mortar, being of a chemical as well as mechanical nature, may be conveniently deferred till some account has been given of the various methods of washing.

Gold Washing.—Whether the gold be obtained from the placer diggings or quartz mines previously described, it is extracted from the earth or vein-stuff by a systematized process of washing, sometimes carried on on a gigantic scale. In the earlier stages of the working of a claim, however, it is usually done by hand, in order to get an approximate idea of the probable yield. It is proposed here to give a brief description of the more simple appliances, together with some account of the application of machinery to the process. The *sine quâ non* of all gold mining operations is an abundant supply of water, without which an otherwise valuable claim may become useless.

Pan.—This simple instrument is employed at all mines in some period of their existence, though when operations are carried on on a large scale, or the pay-dirt is not extremely rich, it is totally inadequate to the requirements of the miners. The pan generally used consists of a shallow dish made of sheet-iron or tin (the former preferred), the bottom of which is flat, and about 14 inches in diameter. The top is about $3\frac{1}{2}$ inches wider, and the pan is about 5 inches deep, it has a general resemblance to an ordinary frying-pan. The miner having placed in it a quantity of pay-dirt, places it on the bottom of a shallow pool about 10 inches deep, and stirs the mud with his hands; after which, removing the pan from the water, he shakes it backwards and forwards, continually allowing small quantities of dirt to pass over the sides. The whole is thus removed, with the exception of gold, stones, and clay. The stones are removed, and after rubbing the clay between the hands a further supply of pay-dirt is added to the remaining contents, and the

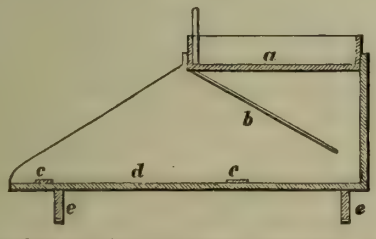
operation repeated. After a succession of similar operations the gold is finally obtained free from everything except heavy black sand, which, after the whole has been allowed to dry thoroughly, is almost completely removed by blowing.

Fig. 15.



Cradle.—It will be obvious from the accompanying sectional diagram that this instrument derives its name from the ordinary child's cot; although now it is comparable to that in size, it appears formerly to have been far larger (from 6 to 7 feet long). It is

Fig. 16.



usually about 3 feet 6 inches long, and 1 foot 6 inches wide, and consists of three essential parts, namely, the sieve or hopper, *a*; the screen or apron, *b*; and the base or sluice, *d*, provided with two transverse strips of wood, *c*, called rifflers, whose office is to retain any particles of gold which may pass through the instrument. The whole is mounted on two wooden rockers, *e*, and provided with a handle, *f*, by which the miner sets it in motion. The sieve, *a*, is movable for cleaning, and has a bottom composed of sheet-iron with holes half an inch in diameter: *b* is composed of coarse canvas, and is serviceable in both retaining particles of gold and compelling all the mud to traverse the whole length of the cradle.

When in use the pay-dirt is shovelled into *a*, and the cradler, kneeling by the side, with his left hand rocks the instrument, while with his right he pours water into *a*. The pay-dirt is thus rapidly disintegrated, and gold, together with heavy sand, &c., being left behind the rifflers, all the remainder is washed away by the current. When large stones occur, however (as is usually the case), they accumulate in *a*, but are not removed till their number inconveniently interferes with the motion. In order to empty the sieve it is removed and the contents thrown out.

When the spaces behind the rifflers are filled, it is of course essential that the whole be cleaned up, as any further gold passing down would be liable to pass over the bars, there being no sufficient projection to retain it; this clearing up usually takes place about three times in the day. *a* and *b* having both been removed, the base, *d*, is scraped with an iron spoon, the whole of the gold, sand, &c., being placed in a pan, by which the gold is extracted as previously described. If there be much fine gold dust, a considerable quantity will collect on *b*, especially if this be made of coarse woollen cloth; from this it is washed into the pan.

The incline of the cradle is usually about 1 in 16 this, however, varies slightly according to the fineness of the gold. The amount washed per day varies from 1 to 3 cubic yards, according to the amount of clayey matter contained. There are almost always two men employed, one who works the cradle, and the other performs all other duties. The ratio of water required to pay dirt washed is about three to one. In consequence of the extensive scale on which operations are now carried on the cradle is now not often met with, but is nevertheless in use among the miners, especially the Chinese in America.

Puddling Tub.—In Australia, where frequently the dirt is very clayey and water very scarce, it is necessary to knead it with water in a tub called a puddling tub, which usually consists of half of a porter cask. The whole is worked up by means of a spade, and when all the clay has been washed away by the water, the remainder, consisting of sand, gravel, and gold, is removed and washed either by the cradle or pan.

Tom.—This instrument is interesting as having been one of the first employed for gold washing on an extensive scale, but having now long been superseded by still more thorough methods it is unnecessary to give a detailed description. It consisted of 2 parts, a "tom" or trough about 12 feet long, and a riffler box. The tom was placed on an incline, (about 1 in 12) and its lower end, provided with a perforated iron grating, placed over the upper end of

the riffler box, which was somewhat less inclined. A constant stream of water entered at the upper end of the tom, and pay dirt being thrown in at this point, was disintegrated in its passage to the riffler box; this box being about 8 feet long, and provided with transverse bars as in the cradle, to retain the particles of gold.

Sluice.—All the methods which have from time to time been proposed are now almost entirely superseded by sluices of various forms, the use of which, in addition to requiring less manual labour, is attended with a far less loss of precious metal. They can, however, only be employed where there is an abundant and constant water supply, and are rarely met with in Australia, but are common in California.

It is usually made of wood, and consists of numerous portions, each about 12 feet long, fitted end to end, each trough tapering slightly so that its lower end may fit into the upper of the next succeeding. These troughs are roughly constructed of sawn timber, and are each provided with a series of rifflers, sometimes transverse only, but more frequently longitudinal and transverse combined. The incline varies from about 1 in 15 to 1 in 8, according to the amount of clay contained in the pay-dirt and the approximate size of the gold particles, being of course greater in proportion as there is more clay. In this case, however, there is more risk of losing small particles, and it should therefore be made longer. The whole sluice is usually several hundred feet in length. It is not essential that the gradient be the same along the whole length; it frequently varies, being great at the upper end, thus facilitating disintegration, while the lower portion is less inclined in order to avoid loss of gold. As in the "tom," a continuous stream of water enters the sluice at the head, at which point also the pay-dirt is introduced. As the dirt passes down the sluice care must be taken to avoid masses of clay escaping disintegration, as not only would the gold contained in them be lost, but they are liable to carry down with them any particles of metal which they may meet in their path. Mercury is introduced at different points in the length of the sluice, which, being retained by the riffle bars, serves to collect particles of gold.

When much of the gold to be extracted consists of very fine particles, an amalgamated copper plate is frequently employed, the whole current passing over it, and the inclination on which it is placed being very slight, it retains the gold. When a sufficient amount of gold has accumulated the amalgam is removed by scraping, the plate being previously warmed to facilitate the operation, and the mercury subsequently expelled from the amalgam by the aid of heat.

When a sluice has worked for about a week it is essential to remove the gold and amalgam which may be contained in it, in order to avoid loss of it either by clay carrying it away or by theft. To perform this "cleaning up," as it is called, the introduction of dirt having been stopped, and water having been allowed to run through the sluice to wash away any dirt, the removal of rifflers is commenced from the top. They are removed for about the space of 40 feet. The current now washes down, and the accumulation against the first remaining riffle bar is removed and reserved for future panning. Similarly all the bars in succession are removed, the trough cleaned, and the rich accumulation obtained panned out. In order to avoid the delay entailed by a cleaning out, sluices are frequently made double, so that one can always be in operation.

Sluices, instead of being provided with wooden rifflers, are frequently paved with rounded stones along their whole length, when they are known as *rock sluices*. This method is especially adopted in *tail sluices*, which being intended solely for the washing of tailings from ordinary sluices, do not require cleaning up so frequently—the fact of having to remove all the pavement for this operation rendering it more tedious than in the former case.

Hydraulic Mining in California.—This process, which consists in washing down immense beds of auriferous deposits by means of a powerful current of water, has been practised in California since 1852, though in more recent years the employment of it has very much extended. The work is now carried on on a gigantic scale, and as the process removes whole mountains of auriferous gravel and deposits them in the neighbouring valleys, great fears are entertained of many of the rivers being blocked up by the tailings which are produced; already disagreements have arisen between the agricultural and mining interests, the destruction of the face of the land being of course detrimental to the former.

Several necessary conditions have to be attended to in the working of mines of this description. Amongst these may be mentioned :—

(1.) The auriferous gravel down to the bed-rock must all be removed.

(2.) This must be accomplished by the aid of water alone, or at times water supplemented by gunpowder.

(3.) The conglomerate must be mechanically disintegrated without interrupting the whole system.

(4.) The gold must be saved without interrupting the continuous flow of water.

(5.) Arrangements must be made for disposing of the vast masses of impoverished gravel.

The first cost in laying out an hydraulic mine is generally very great, and as a tunnel is usually necessary to lead away the tailings, the operations are not remunerative until after several years' labour. The incline of these tunnels is generally from 5 to 6 inches per 12 foot run, and they are about 7 feet wide and 8 feet high for a single sluice, the exact dimensions depending on the amount of water available.

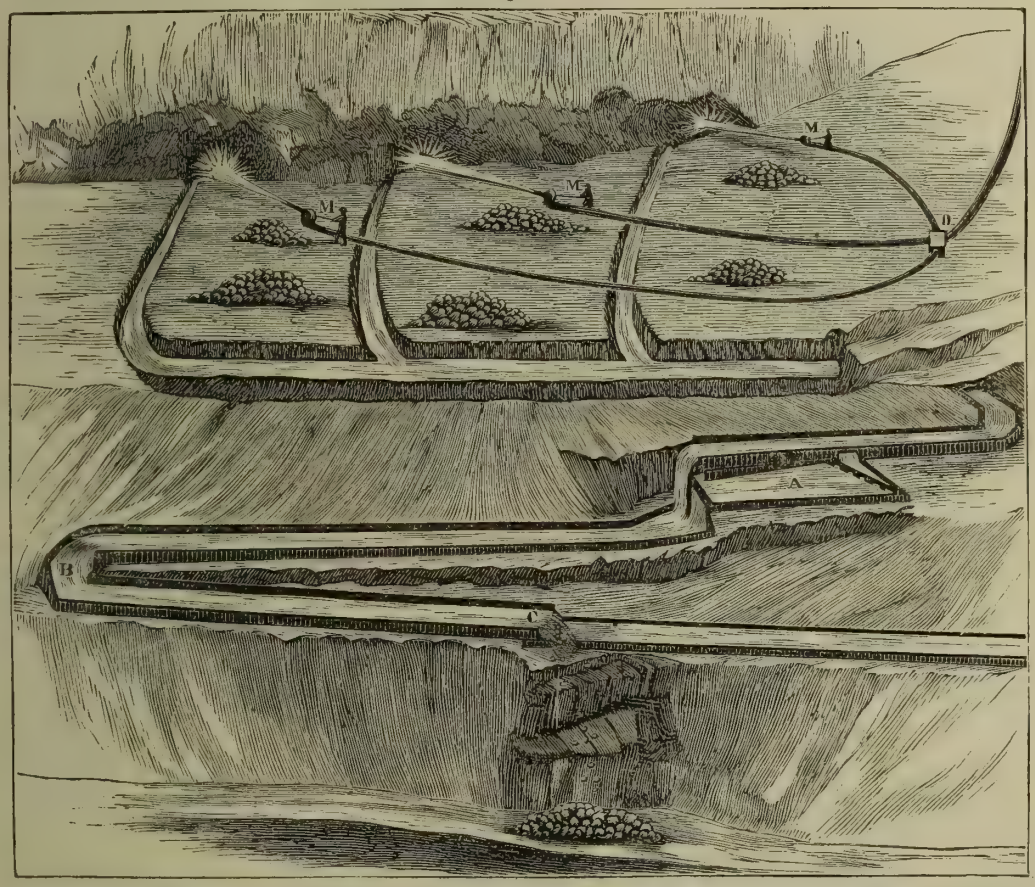
The tunnel must be in the bed-rock, in order to insure all the tailings being carried away; for if auriferous gravel were worked at a level *below* the tunnel, it would of course fail to answer the required purpose. The upper end of it may be connected with the surface in various ways—by an inclined "chimney," a vertical shaft, or a series of terraces, according to circumstances. The external series of sluices leading directly into this opening connect it with the several points at which the gravel is being displaced by the streams of water.

The accompanying engraving, Fig. 17 (taken from the United States government report on "Mines and Mining"), gives a clear idea of the process of hydraulic mining as carried on in California in 1872. The general arrangement will be understood from the foregoing remarks; but four portions require special description—namely, A, the undercurrent, B, the drop; C, the "grizzly;" and D, the distributor.

The *undercurrent* consists of a flat shallow platform of from 500 to 1000 square feet in area, placed slightly below the main sluice box, and somewhat on one side. An opening about 16 inches wide is cut in the sluice, in which are inserted steel bars, about 1 inch apart. Underneath is a conduit, which leads such liquid and particles as pass through on to the platform, where it is all distributed by means of the series of checks seen in the engraving. The incline of this platform is about 1 inch to the foot, and it is provided at its lower end with an opening to return the bulk of the material to the main sluices below. Frequently at the point at which these two currents join, the main sluice is made about 4 or 5 feet deeper than its average depth, an arrangement which is found of great service in arresting amalgam, &c. The main advantage of undercurrents is the fact of their catching particles of gold, &c., which would otherwise frequently pass away with the tailings.

The *Drop* acts in the same manner as the terraces,

Fig. 17.



sometimes used in place of the chimney for connecting the tunnel with the exterior, that is, it causes masses of earth, &c., to be broken by the fall. It is generally considered advisable to divide a given drop of, say, 100 feet into several small ones, rather than retain it as one large one, the disintegrating effect being greater.

The *Grizzly* is a grate or framework of parallel iron bars with interstices, used here and there in a line of sluice boxes, in order to throw out large pebbles or stones, thus permitting only those smaller particles which can pass through the interstices to continue their course down the sluice. This arrangement is only useful when the sluice box passes near the edge of a steep embankment, down the sides of which the stones can be readily got rid of. The action is obvious from the engraving.

The *Distributor* is a strong cast-iron box, which receives all the water required for the mining operations, and which distributes it to the several nozzles or "monitors." It is provided with two or more openings, closed by strong iron gates which are raised and lowered by screws. By this means the water is directed along whichever of the hoses which may be in use. The distributor must be firmly fixed to the ground.

It is frequently necessary in the course of mining operations to resort to blasting when the rock is too hard for the water to disintegrate, in order to open

out fresh masses of gravel, on which the stream of water can act. The mass of water directed against the gravel is immense, and four nozzles, each delivering about 50,000 cubic feet of water per hour, on the same bank may frequently be met with. The quantity of mercury employed is also very great, as much as 2 tons being required to charge a single long sluice. In order to show how great is the economy of working with this process, it may be mentioned that the cost of washing 1 cubic yard of auriferous gravel is

With the pan,	15·00	dollars.
" rocker,	3·75	"
" long-tom,	·75	"
" hydraulic process,	·10	"

Extraction of Gold in Brazil.—At the Morro Velho mine the gold generally occurs accompanied by iron pyrites, the vein stuff being quartz. From this it is extracted in a manner very similar to that practised in California, which has been already described. In place, however, of passing through a stone breaker, the rock is, on being raised to the surface, spread out on "spalling floors," where it is broken by means of cast-steel hammers and sorted, rocks which are known to be comparatively poor being thrown aside. The workable ore is then supplied to a stamping mill. On passing out of the mill the finely-divided ore comes directly in contact with the amalgamation plates, &c., in California, while in Brazil it is led over skins tanned with the hair on, and baize cloths, laid in inclined sluices called "strakes," about 30 feet long, and having a fall of 1 in 12. These skins and cloths are from time to time removed and washed in tanks of water, in which the particles of gold, together with a portion of the vein stuff, are collected. This concentrated ore is separately subjected to the process of amgamation.

Extraction of Gold in Hungary and the Ural.—In Hungary, the ore, after being stamped in mills similar in their general construction and arrangement to those already described, passes into a series of amalgamating pans. On emerging from these amalgamators, the slimes, which still contain a very perceptible amount of gold, are distributed over a series of inclined planes covered with cloths, by means of which much of the remaining gold is collected by washing from time to time in tanks, as in Brazil. The slimes are then concentrated by means of settling pans and shaking tables (the latter of which are somewhat peculiar in their construction), and after being thus enriched they are treated as original ore. The rich slimes collected on the inclined planes are still further concentrated by washing on an inclined plane, down which a stream of water always passes, the mud being brushed up the plane against the stream; the richest portion thus obtained, after having been concentrated by washing in a peculiar shaped pan held in the hand, is amalgamated by agitation with mercury.

Among the different methods adopted in the Ural districts, there is one by Agté, in use at Alexandrowsk, which is precisely similar in principle to that above described, though somewhat more complex in the arrangements. In this process a conical cylinder of sheet-iron is employed, about 8 feet in length, and having a mean diameter of about 3 feet 6 inches. It is pierced with holes about half an inch in diameter, and is fixed on a spindle communicating by a train of wheels and shafts with a water-wheel, horse gin, or any other prime mover, from which it is capable of receiving a rapid rotatory motion, so as to make from thirty to forty revolutions in a minute. A crank on the shaft which communicates motion to the cylinder works a double pump at the back of the frame, which raises water from a well or some other convenient reservoir to the cistern, and from this it is conducted by pipes into each end of the cylinder. The ends of the cylinder are open, and the pipes are so arranged as to diffuse the water pretty equally over its interior surface. Nearly on a level with the top of the arrangement is a line of rails, on which the auriferous sands are brought in waggons to the hopper, from which they fall into the smaller end of the revolving cylinder. The latter by its centrifugal action ejects through its numerous perforations the water and finer particles of sand and gravel, which are received upon the inclined platform below, whilst the larger fragments are carried down to the under end of the cylinder, and there fall into a box. Any gold nuggets which may be mixed with these fragments, being well washed and burnished in their gradual progress through the cylinder, are now readily perceived and picked out. The platform, which receives the water and auriferous sand expelled through the holes in the cylinder, is provided like the cradle, or sluice just mentioned, with numerous cross bars, for the purpose of checking the current, and arresting the heavier particles of the ore; and after traversing this platform, the current descends to a concave table or tye, which is also furnished with a series of wooden bars at intervals of 2 or 3 feet. The sands which have arrived at this part of the machine are kept constantly stirred by square frames carrying blunt iron knives, and suspended by vertical bars from a wooden axis above the tye, and placed in the direction of its length. The frames are made to fit into the cavity of the tye, and a swinging alternating motion is given them by means of the rods. In this way the sands are well stirred; and while the heavier or richer portions are retained and accumulated behind the check-boards, the lighter materials are carried away by the current at the lower end of the tye or buddle, from which, if not sufficiently impoverished, they are received on a fresh series of tables, furnished with similar agitating apparatus, and are finally allowed to pass off. This machine operates on 200 tons of alluvial sand in the course of an ordinary working day of ten hours, with the labour of twenty men and six boys, including ten men for removing the waste, if in a level country, without advantages for otherwise clearing it away.

The partitions in the bottom of the tyes are ribs of 2 inches high and $2\frac{1}{2}$ inches wide, held by screw-

bolts and nuts, and are removed every now and then for the washing out of the concentrated auriferous sand. This is done the more frequently in proportion as the sands are richer in gold.

Fine Washing. — The gold obtained from the preceding operations is still so much mixed with sand and other substances, as magnetic iron, pyrites, &c., that it requires to be further concentrated, either by additional washing or by amalgamation. The powder collected in the buddles or tyes is commonly of a grey colour, and is termed *grey schlich*. By the cylindrical machine above described, the original ore or auriferous sand is concentrated to about 3 tons of schlich for every 200 tons of the crude material employed. For its further cleaning and concentration by washing it is treated on uncovered tables or frames, 7 to 10 feet long, by 3 or 4 broad, and divided into an upper and lower part by a lath nailed across the bottom. Also, across the upper part are fixed two boards, which regulate and equalize the flow of water. The schlich to be washed is placed upon the upper division, and the workman, standing upon the frame in wooden shoes, mixes the sand with the water, and gently moves it against the current, towards the head of the arrangement, with a small wooden hoe or broom. The gold thus arranges itself chiefly near the head-board, and when a certain amount is collected, he rakes it with his hoe or broom just strongly enough to draw down the earthy particles over the lath to the lower division, without disturbing the heavier and richer deposit. This delicate operation requires skill and dexterity, and must be continued till all the coarse fragments are removed, after which the flow of water is reduced. The workman by light brushing raises again all the slime which may still remain, and as much as possible of the magnetic iron ore, and takes up as the product of his manipulation the *black schlich* which is left. The upper portion of the box being thus cleared, he now brings upward that which has settled in the lower part, and passes it one or more times through the same operations. This process, for which the most skilful and experienced workmen are required, is termed *fine washing*. The black schlich or ore thus concentrated is dried, and is freed from a further quantity of magnetic iron by the use of an artificial magnet or a piece of loadstone.

The *gold-troughs* used in Hungary and Transylvania for the final washing of the powder or schlich obtained from the cloth-covered tables already alluded to, as well as the process of washing, are similar to those just described. In these countries a broom of heather or birch is generally used instead of the hoe; and in Transylvania the troughs, which are of larger dimensions, are fitted with two traps in their channels, into which the different qualities of schlich are swept at different stages of the process. Even after this fine washing, the resulting products are sometimes further concentrated in the bowl or washing-pan, and so reduced to a state fit for melting, or they are subjected to the process of amalgamation.

Amalgamation of Gold Ores.—Although some of the gold of commerce is imported in the shape of dust, or small grains extracted from the auriferous soil by simple washings without the aid of mercury, yet by far the greater amount of the precious metal is obtained by the various amalgamating machines, the action of which depends on the well-known affinity existing between mercury and many other metals when clean surfaces are presented to each other; for, as will presently be seen, if the gold has any protecting covering by which the mercury is prevented from attacking it, amalgamation does not take place, and serious loss may result.

It may be laid down as a general rule that amalgamation would be advantageously resorted to in all cases, as the finishing process in those operations which precede the metallurgical treatment of gold. By no other method can the precious metal be so thoroughly extracted from the gangue; and so effective is its action, as compared with mere washing, that it has often been applied with success to secure a remunerative return from the refuse or waste sands which have passed through the gold-digger's cradle. Its profitable application, however, will depend on the nature and richness of the auriferous soil. If the gold is abundant, and is found in considerable grains, the greater and most valuable part of it is readily separated, and easily concentrated sufficiently by mere washing. On the other hand, if, as often happens, the gold is diffused through a dense and heavy gangue, in particles so minute as to be invisible to the unassisted eye, it is evident that these particles will float away with the current when the sand or crushed ore is washed on inclined tables, and that their extreme minuteness will counteract the effect of that difference in specific gravity by which it is so easy to separate the larger grains when diffused through a less dense soil. On the whole, therefore, while amalgamation must be applied in all cases where it is desired to extract, practically, the whole of the gold, it is more especially applicable to its extraction from quartz rock, from heavy pyritous ores, and from other descriptions of gangue, through which it is diffused in a state of extreme division. And as the mercury exerts no chemical action, but may be again separated from the gold with little loss, the advantages afforded by the great efficiency of this process are not materially restricted by economical considerations.

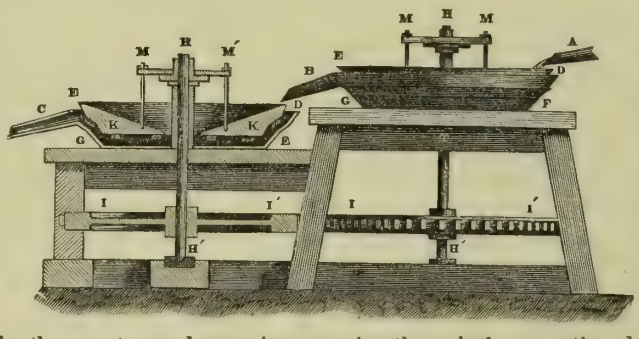
The form given to the amalgamating machine varies considerably in different countries; it may be well therefore to briefly describe a few of the more important.

In Piedmont, where veins of auriferous pyrites have been worked from a very remote antiquity, the extraction of the gold is effected almost entirely by amalgamation. The produce is very variable in different localities, but averages about twenty shillings in value from 150 pounds avoirdupois of the auriferous ore. The amalgamating mills are erected in great numbers on the banks of the various rivulets which traverse the mountains. These establishments usually consist of small wooden buildings, each of which contains four amalgamating machines, and

they are erected at intervals over the whole length of the valley of Anzasca, from Champnaga to Pie di Mulera.

The ore or mineral, when extracted from the mine, is first subjected to a grinding or triturating process in a machine resembling in its action and operation the common millstone, and driven by a water-wheel. When thus reduced to powder, it is carried off by a stream of water to the amalgamating mills, represented in Fig. 18. Whilst held in suspension in the water, it is conducted first to the upper mill by the spout A, from this to the second

Fig. 18.



by the spout B, and so on in succession through the whole series. Each mill consists of a cast-iron basin, D E G F, fastened by screws to the top of a strong frame or table, and fitted in its centre with a tube, traversed by the axis, H H′, moved by the toothed wheel, I I′, and with which revolves a wooden muller, K K, fixed to the upright spindle by the iron collar, M M′. This movable part of the mill has externally the same form as the internal cavity of the fixed iron casting, G, in which it revolves horizontally, at the distance of about half an inch from its surface; at the same time it is furnished with several iron ribs, which come nearly in contact with the interior of the casting. The rotating muller is made of hard wood, and is hollowed out like a funnel, in which the auriferous slime accumulates, and gradually penetrates into the interval between its external surface and the bottom or interior surface of the iron basin, and from this it flows to the next mill by the spout, B or C.

In the bottom of the fixed vessel is placed about half a hundredweight of mercury, which has a depth of half an inch; and when the machine is set in motion the pounded mineral is constantly agitated and mixed with this fluid metal by means of the iron ribs nailed to the bottom of the muller. The minute particles of gold are thus immediately dissolved and taken up by the mercury, while those which escape amalgamation in the first mill are arrested and retained by the second, third, or fourth of the series.

After working the mills continuously for several weeks, the time required being longer or shorter according to the richness of the mineral under operation, and when the mercury is judged by the workmen to be sufficiently charged with the precious metal, the mills are stopped, and the amalgamated mass is taken out. It is important not to protract the process unnecessarily, otherwise a serious loss of mercury is sustained, occasioned, perhaps, by its partial conversion into a sulphide, which is carried away with the current. The mercury, when drawn off, is washed, and then strained or filtered through a piece of chamois skin, for the purpose of obtaining the solid amalgam, which usually contains about one-third of its weight of pure gold. This is separated from the quicksilver by distillation in an iron retort, the beak of which dips into a vessel containing water. The whole of the mercury united with the gold is thus recovered, and the only necessary loss is due to the carrying away, by the current, of mercury in the form of sulphide. Dumas states that the loss incurred in this manner is equal to about one-fourth of the quantity employed; but so large a waste must result from careless manipulation.

At the Schemnitz works in Hungary, the slimes, after leaving the stamping mills, pass directly into amalgamators similar to those already described, of which there are, however, only two in each series, the slime passing out of the second on to inclined tables, as already mentioned. Only half the amount of mercury is employed, and in eight mills the loss is only about 3 ozs. of mercury per month.

In the Salzburg Alps the method adopted for the extraction of gold is peculiar, and consists of three distinct operations, washing, roasting, and amalgamation. As the annual produce, however, is quite insignificant (only about 65 lbs. per annum), it is unnecessary to describe its peculiarities further than to say that, prior to passing into the amalgamators, the slime is ground in a mill very similar to the common flour mill.

Revolving barrels are employed for extracting gold from the concentrated slimes obtained, as already described, at the Morro Velho mines in Brazil. These are very similar in construction to those used at silver works, and which will be described in the article on that metal. After the mixed slimes and mercury have been in the revolving barrels about thirty hours they are run off into a trough or "saxe," divided by transverse partitions; in each division of which a rake moves backwards and forwards, by which means the rich amalgam collects on the bottom, the impoverished slime being run off on to the "strakes" already described, by which it is enriched prior to being again introduced into the barrels.

Amalgamation has been brought to a high state of perfection in California, and as in Australia very similar arrangements are employed, a description of the American method will suffice. This description is derived mainly from the annual report of the United States Commissioner of Mining Statistics for the year 1872. On emerging from the stamping mills (where a preliminary amalgamation on copper plates frequently takes place), the slimes pass over an apron of amalgamated copper plates, by which

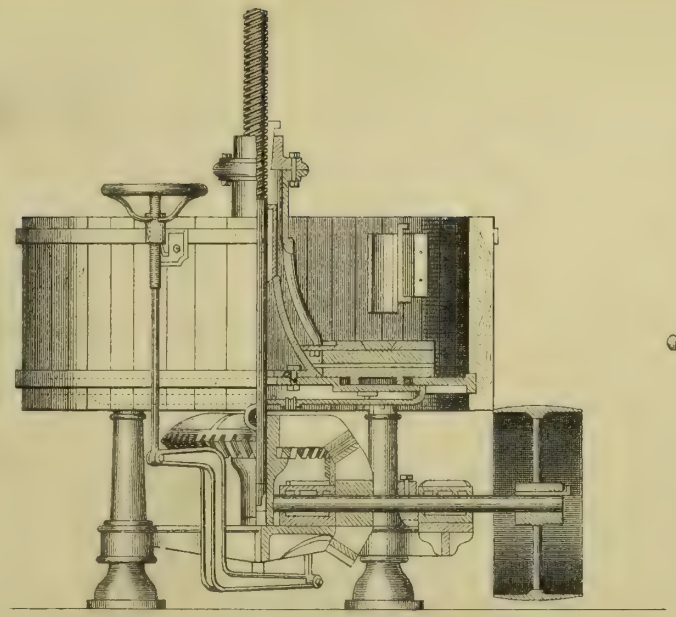


Fig. 1.

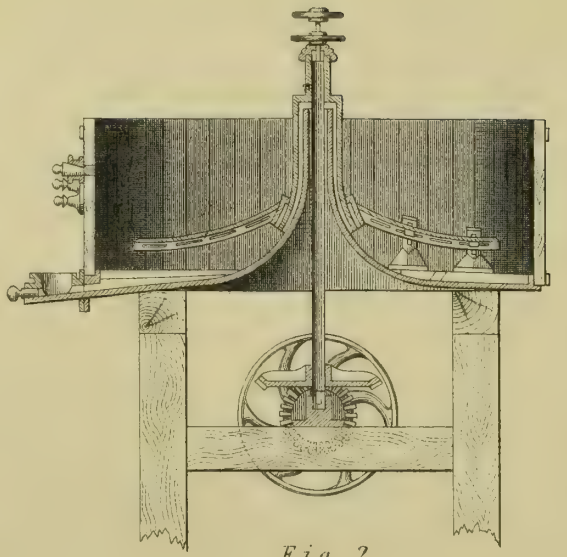


Fig. 2.

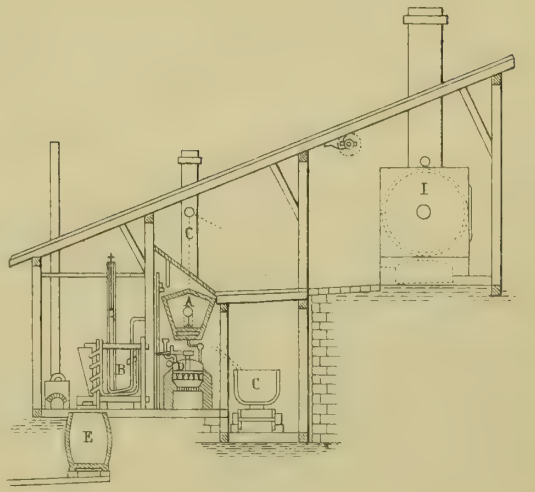


Fig. 3.

Fig. 4.

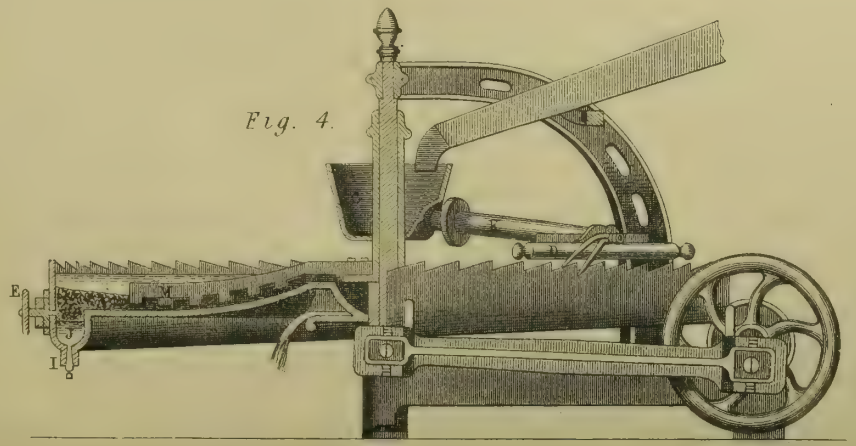
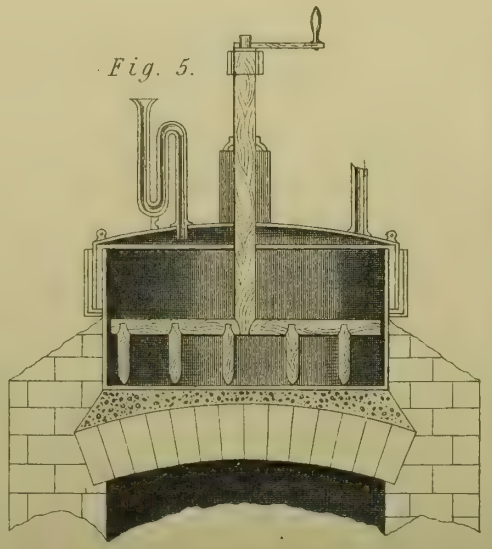
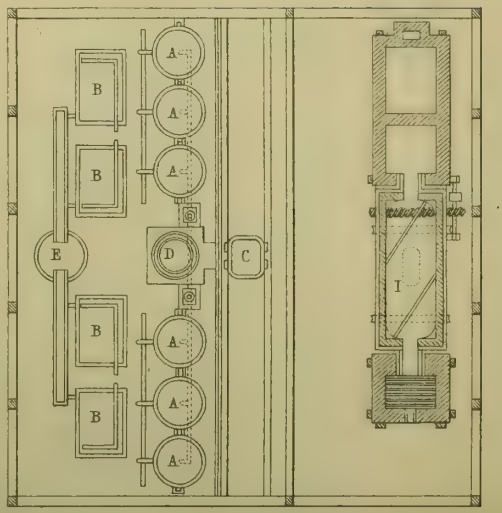


Fig. 5.

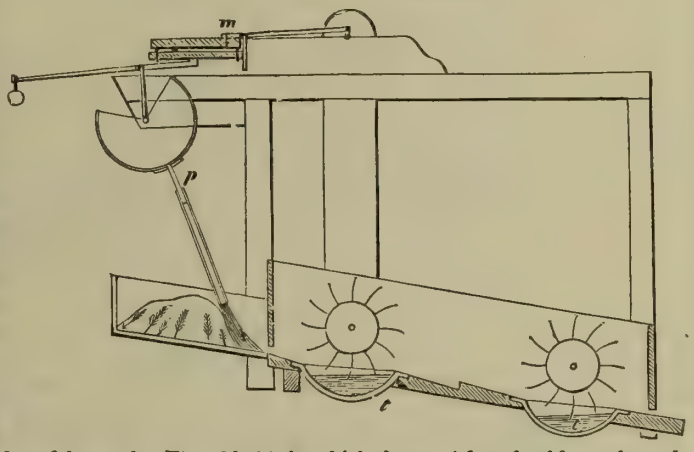




means a considerable quantity of metal is removed, and thus prevented from passing down the sluices which immediately succeed this apron. To every mill of four or five stamps there are three sets, each consisting of two sluices, together about 16 feet long, and having an incline of about 1 in 16. They are covered with blankets, two sets being used at a time, while the third is employed when the blankets of either of the others are being washed; the washings from them are introduced into an amalgamator which may vary in construction; that usually employed is known as Atwood's amalgamation, and is represented in elevation in Fig. 19. It consists of two hollow, cylindrical troughs, *t*, *t*, about 18 inches long, of wood or iron, filled with mercury. The washings are swept from a box at the head of the apparatus over these troughs by a current of water heated to about 120° Fahr., where they are agitated by wooden cylinders provided with arms of such a length as just to touch the mercury, and rotating in a direction opposed to the current. By a system of levers, shown above at *m*, the pipe, *p*, which supplies water is caused to rotate in such a manner as to secure a regular supply of washings to the troughs, on leaving which the stream passes over a series of riffles filled with mercury. The skimmings removed from time to time from the various parts of this apparatus are ground and amalgamated in pans which vary much in their details of construction. The forms most employed at the present day are those designed by Patton, Wheeler, Cox, Horn, and Booth & Co., and the arrangement of a Wheeler pan is shown in Fig. 1, Plate I. It consists of a shallow cylindrical basin of wood or iron, about 4 feet in diameter, and 18 inches deep, provided with a flat iron bottom, to which dies are attached, and beneath which is a steam-chest, in order to be able to heat the contents when necessary. From the centre rises a conical tube in which a vertical shaft, carrying a "muller-plate," rotates, receiving its motion from bevel gearing below. To the muller-plate are fixed shoes at intervals, and the distance between these and the dies can be adjusted by a hand-wheel at the side of the pan, which, through a lever, raises or lowers the steel block in which the extremity of the shaft rotates. The removal of the muller from the pan for the purpose of cleaning is accomplished by running it up a screw on the shaft. When the Knox pan is used 100 lbs. of skimmings are introduced, and water added until the pulp just adheres to a stick. After about three hours' grinding the temperature is raised by heating the steam chest, and a cupful of equal parts of saltpetre and sal ammoniac is added, together with about 5 lbs. of mercury. After three hours further working water is added and a few handfuls of caustic lime, when the diluted pulp, now nearly filling the pan, is stirred for about twenty minutes and discharged, without stopping the motion of the muller, first from an upper, and subsequently from a lower plug-hole. This pulp, which frequently contains as much as 100 dols. of gold per ton, passes into an appliance very similar to a pan, called a settler, and shown in section in Fig. 2, Plate I. This is a circular box, in which revolves a central axis carrying arms, and to these iron shoes are attached. The shoes do not come in contact with the bottom, but are faced with wooden rubbers, in order to keep the heavier parts of the pulp thoroughly stirred. Water is introduced during the operation, and the thinned pulp can be drawn off at plugged holes from time to time. An iron bowl to contain mercury is attached, communicating with a radial gutter cast in the iron bottom of the settler. The sulphurets, &c., recovered by this process, are treated by the chlorination process presently to be described.

The sands, after passing the blankets, and also those from the amalgamators, discharge into the Eureka rubbers, shown in plan and part section in Figs. 20, 21, in which the particles of gold are cleaned and brightened by rubbing, and are to some extent collected by means of amalgamated copper plates. The apparatus consists of a rectangular cast-iron box, A A, 7 inches deep and 4 feet 8 inches square, provided with a false bottom of cast-iron dies or plates, *b*, *b*, *b*, alternating with strips of soft wood, *c*, *c*, *c*, on which cast-iron shoes, *d*, *d*, *d*, fastened to a wooden frame, B, receive a rectilinear motion by rods connected with an eccentric. Beneath these shoes are fixed wooden boards carrying amalgamated copper plates. The eccentric makes about fifty-five revolutions per minute, and one rubber is sufficient to treat the sands from four or five stamps. On leaving the rubbers the sands pass over amalgamated copper plates from 20 to 30 feet in length, and having a gradient of 1 in 24.

Fig. 19.



The amalgam obtained is purified by being rubbed in iron mortars with the addition of mercury, a current of water being at the same time caused to pass over it, and everything so removed is returned to the pan. The resulting amalgam is then squeezed through canvas bags, and the mass left transferred

to a furnace, by means of which the mercury is driven off as presently to be described.

Sodium Amalgam.—It has been already mentioned that the amalgamation is frequently hindered, or altogether prevented, by the fine particles of metal being covered by a thin film of a protective covering. This tarnish generally consists of compounds of sulphur, arsenic, antimony, bismuth, or tellurium, or simply grease. Dr. Wurtz, in America, and Mr. Crookes, in England, at about the same time (1864–65), discovered that, by the addition of a small quantity of sodium to the mercury, amalgamation is very much facilitated, even if the gold be admixed with any of the above-mentioned substances. Dr. Wurtz recommends two amalgams, one containing 2 per cent., and the other 4 per cent. of sodium. The latter is a solid, very brittle, crystalline substance. By the addition of 1 per cent., or even less, of either of these to the mercury used for amalgamation, it is said to adhere to metals which otherwise would not have been "wetted" by it. Crookes recommends three kinds, which he calls the A, B, and C amalgams. Each contains 3 per cent. of sodium. In A, however, it is mixed with 97 per cent. of mercury; in B with 77

Fig. 20.

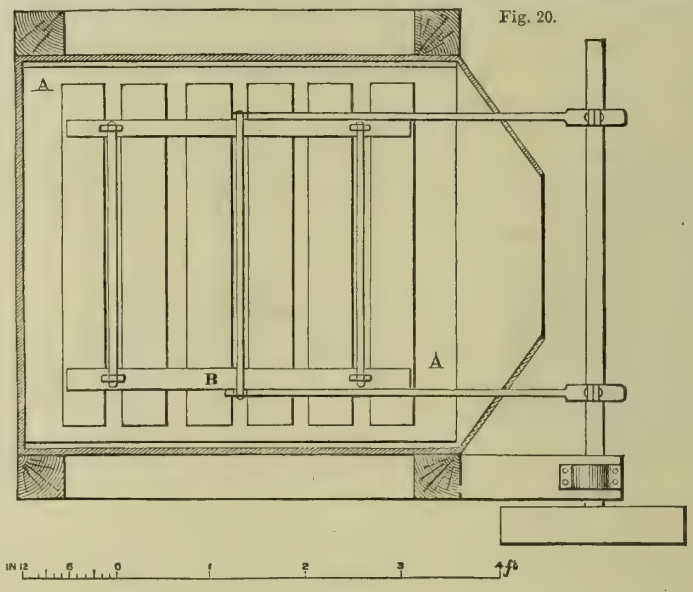
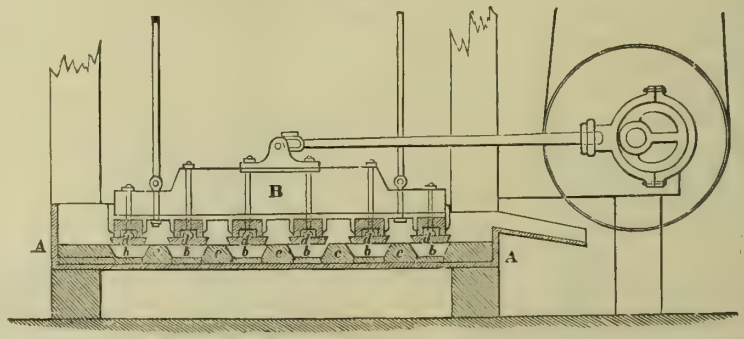


Fig. 21.



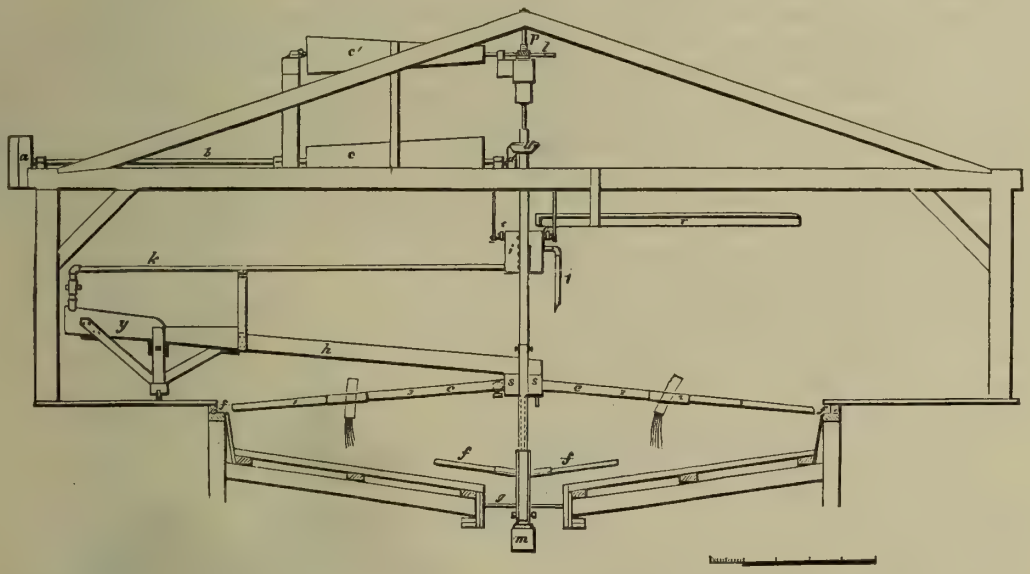
per cent. of mercury and 20 per cent. of zinc; and in C, with 77 per cent. of mercury, 10 per cent. of zinc, and 10 per cent. of tin. In preparing these amalgams the mercury is heated to about 300° Fahr., and care must be taken to add the sodium in very small quantities at a time, as the reaction which takes place is very violent. In the case of B and C the sodium is added to one half of the mercury, while the other half is mixed with the other metals; the two halves are then fused together.

Concentration of Tailings.—The impoverished sands and ore which pass off from the sluices, &c., are subjected to a process of concentration, in order to collect the small particles of gold inclosed in pyrites and other metallic sulphides, which would otherwise be lost. There have been many contrivances employed for this purpose, but it is unnecessary here to do more than briefly describe the plan generally employed in California at the present day. On leaving the sluices the sands pass into a simple apparatus called a *pointed box*, by means of which they are sized, as subsequent operations are found to be facilitated by the sands operated on being of a uniform size. They are next roughly concentrated by being passed over sluices with movable gates at their lower ends, which act the part of riffles. The final concentration is performed,

on the small scale, by rockers worked by hand, and on the large scale, by an apparatus called a *buddle*, or by Hendy's concentrator. Buddles are of two kinds, convex and concave, both extensively used, but the latter only will be described.

The *rocker* consists of a simple wooden trough, about 10 feet long, and resting at each end on supports, so that it can be rocked in a manner similar to the cradle already described, the incline being about 1 in 12. The concave buddle of Paine and Stevens is shown in section in Fig. 22. It consists of a circular wooden table, about 18 feet in diameter, slightly inclined inwards, in the centre of which is an opening about $2\frac{1}{2}$ feet in diameter. From the centre of this opening rises a vertical shaft, to which a rotatory motion is communicated by mill gearing above, and to which several appendages are attached. These are *g*, a self-raising riffle pulley, to which an upward or downward motion can be given by means of a rod passing upwards, and connected with an

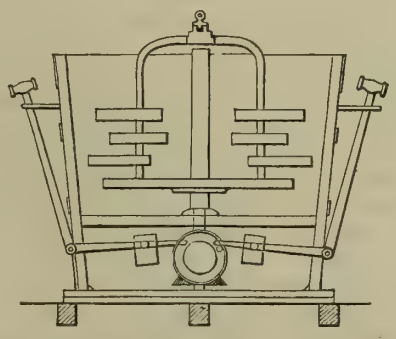
Fig. 22.



endless screw at the top, the arms, *f f*, carrying the brushes, and the sand distributing troughs, *e*, *e*. The sands having been placed in the box, *y*, are washed by means of water led from the trough, *i*, by the pipe, *k*, into the sieve, *z*, whence they pass along *h* to the troughs, *e*, *e*. As these rotate they distribute the sands round the circumference of the buddle, where the heaviest particles remain, the light ore finding its way to the centre, the brooms attached to the arms, *f f*, maintaining an even surface of sand. When a sufficient quantity of ore has been introduced the whole mass on the surface of the buddle is divided into three concentric rings. That in the interior is thrown away as waste, the middle portion is gradually washed by a stream of water descending from the distributing troughs as shown, and which can be led on to the buddle at any distance from the central rotating shaft. The sulphurets, &c., left after this operation are added to those at the outer circumference, the whole being again passed through the buddle in order to further enrich it. These headings are subjected to a final process of cleansing called *tossing*, when it is intended that the gold shall be extracted by chlorination. The nature of this apparatus will be at once understood from the accompanying sketch, Fig. 23. It consists of a tub into which the sulphurets, &c., are introduced, and in which a number of flat iron horizontal stirrers rotate, the sides of the tub being at the same time struck rapidly by means of hammers.

The tub is half filled with water, and when the stirrers have been set in motion, making forty-eight revolutions per minute, the ore is shovelled in near the periphery. When nearly full the yoke carrying

Fig. 23.



the stirrers is raised, and the hammers are set in motion to induce the rapid settling of the sands. The water is now removed, and the sands, having a depth of about 13 inches, are divided into three lots. The upper 2 inches are thrown away; the next 5 inches are retossed, and the remainder is sent to the chlorination works. When Hendy's continuous concentrator

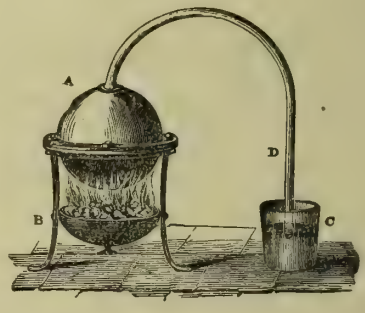
is employed it is not usually necessary to use the pointed box, nor previously to concentrate by self-raising riffle-boxes. The concentrator is shown in Fig. 4, Plate I., and consists of a shallow pan 5 or 6 feet in diameter, supported by a vertical shaft in the centre, and made to oscillate by cranks on one side, which are joined by connecting rods with the periphery of the pan, and this turns upon a vertical axis through a short distance for every revolution of the crank shaft. The bottom of the pan is raised in the centre to nearly the height of the rim, in order to facilitate the movement of particles towards the circumference. The machine must be carefully levelled, and the tailings, direct from the blankets, are delivered by a trough to the hopper, C, from which they pass through the pipe, K, and distributor, D, into the pan near its outer edge, and the rotation of D by means of two pawls attached to it, and acted on by teeth on the rim of the pan, causes this delivery of the tailings to take place evenly at all parts of the circumference. Rake-like arms, M, rotate with D, in order to stir the compact mass of sand, &c., which settles at the bottom. The crank makes 210 revolutions per minute, and the accumulated sulphurets are discharged through the gate, E, while the amalgam and mercury collect in the depression, J. Each machine concentrates 5 tons of tailings per twenty-four hours.

The process at present in use in California for concentrating tailings cannot, however, be considered as satisfactory, and a good concentrating machine has yet to be invented.

Plate II. shows the general arrangement of a gold mill, and from it a clear idea will be at once gathered of the several processes which intervene between the raising of the ore and the final escape of the waste sands, &c., into the tail-sluices. The ore is thrown down in front of a Blake's rock breaker, and after leaving it passes down an incline to the self-feeder, and thence to the stamps, where amalgamation often takes place. In front of these is an apron of amalgamated plates, and beyond are the blanket-tables where the pulp undergoes mechanical preparation, the resulting two qualities being differently treated. The sands which pass over are received in Hendy's concentrator, and after being a second time concentrated, pass into the tail-sluices. That which remains on the blankets is washed into tanks, then passed through Atwood's amalgamators and over copper riffles, and finally also reaches the second concentrator. Below the concentrator in the figure are seen a Wheeler's pan and settler. The pyrites obtained on the concentrators is usually roasted and treated by chlorination.

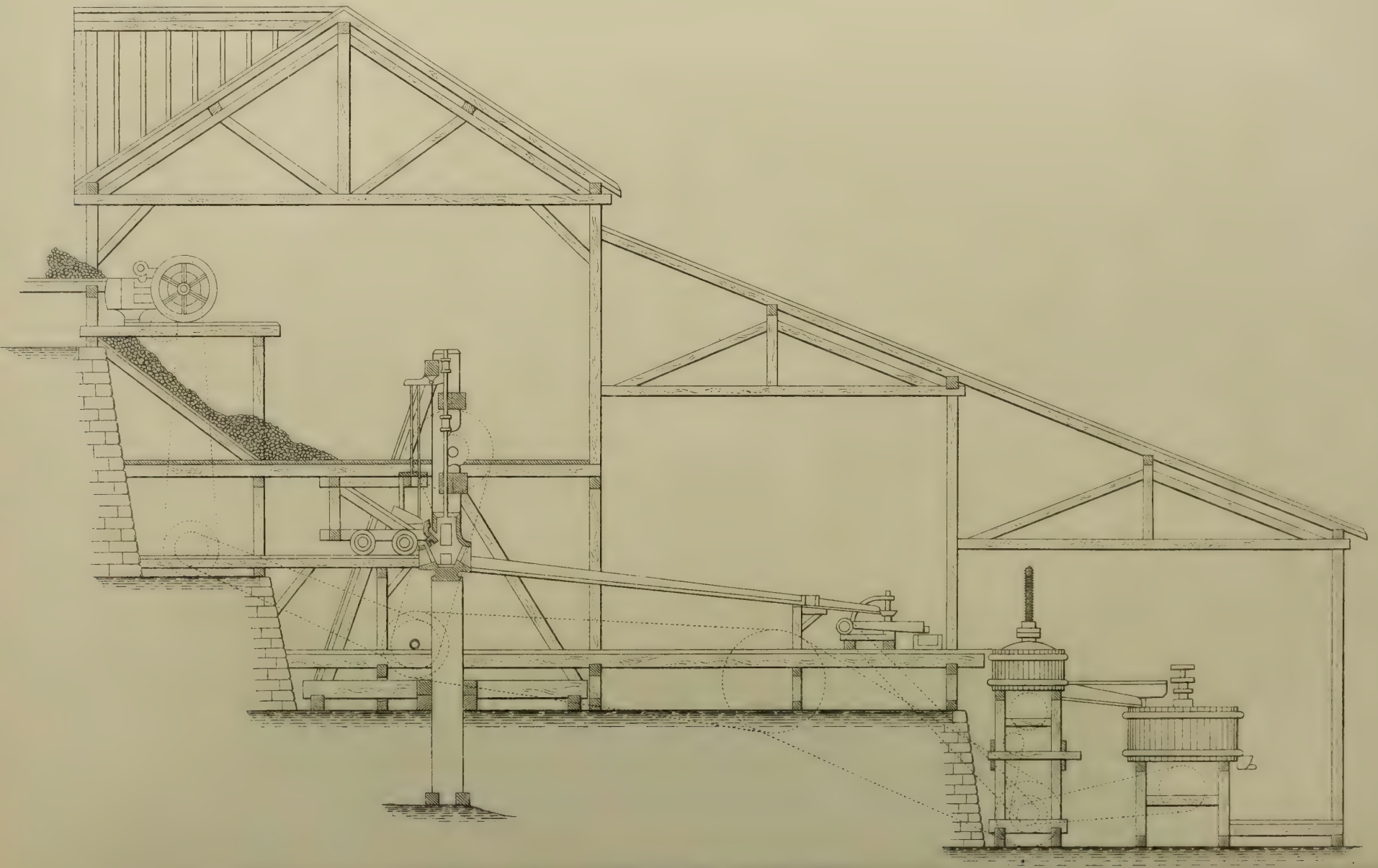
Distillation of the Mercury.—When the amalgam has been formed by any of the methods or machines above described—in all of which the object kept in view is to place the particles of gold in the most favourable condition for coming into contact with the mercury, and combining with it—and when the fluid metallic mass has been washed, and the excess of uncombined mercury strained off, the last operation required in this method of treatment is the separation of the mercury which remains with the gold in the form of a semi-solid amalgam. This is performed by distillation at a high temperature, in a cast-iron vessel prepared expressly for that purpose. Different forms may be given to the apparatus, according to the scale on which the operation is conducted; but a very convenient one is that represented in Fig. 24, where A is a cast-iron sphere or shell made in two parts, and capable of being joined together in the middle by a flange and screws. From the top of the upper hemisphere proceeds a bent iron pipe, D, which dips into water contained in the vessel, C—the whole forming a convenient iron retort. When used, the hemispheres are taken asunder; the amalgam is introduced, and the two halves are again screwed together and well luted with some refractory substance. The retort is then placed on any convenient support over the fire, B, which may be of wood or coal; the heat is gradually

Fig. 24.



raised, and the sublimed mercury, which is conveyed away by the tube, D, is condensed and collected in C. Care must be taken to prevent the end of the pipe from dipping too deeply into the water; for if the temperature of the fire happens to fall, a partial vacuum is produced in the retort, which, if the pipe be too deep, will cause the water to rush up into the globe, and produce an explosion. The end of the pipe is, therefore, introduced just below the surface of the water, so that if a small portion of the water be drawn up into the pipe, that which remains in the condenser, C, immediately sinks beneath the level of the orifice, and all danger is averted.

In California a cast-iron cylinder about 11 inches in diameter, and from 4 to 5 feet in length is used, and the amalgam is introduced in cast-iron pans. A retort of the above dimensions is capable of receiving five such trays containing 270 ounces of amalgam each. The mercury condenses in an iron pipe, surrounded by water, which is attached to the top of one end of the retort, and dips into water at its outer extremity. The retort is set nearly horizontal, the pipe passing out at the lower end, while the upper end is provided with an air-tight lid held in its position by a clamp. Heat is now gradually raised, and should never be allowed to exceed a dull red heat, as the gold is liable



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to contract, and thus retain mercury: several hours' exposure to a low temperature is far more effective in driving off the last traces of mercury than a shorter time with a high temperature.

When the distillation is concluded, which is known by the cessation of any further accumulation of quicksilver in the condenser, this distilled mercury is collected to be used for future amalgamations. The gold which remains in the retort, A, is now comparatively pure; but still contains a mixture of silver, copper, or other metals, in greater or less proportion, according to the sources or localities from which it has been procured. The separation of these, with a view to the obtaining of the gold in a state of absolute purity, will form the subject of the next portion of this article.

In the meantime it may be repeated that the amalgamating process is chiefly applied in the working of auriferous veins, or *gold-mining* properly so called, in contradistinction to the much more common method of extracting the gold from drift-beds or stream-mines, by the mere operation of washing. In the former case the gold, generally in very minute particles, is mingled with various other minerals and rocks, as pyrites, zinc-blende, quartz, &c., and can only be extracted after the whole has been reduced by stamping to a very small size—in which state the gold, often so minute as to be invisible, would be almost entirely carried away by a stream of water. It is here therefore that amalgamation offers peculiar advantages, as the mercury seizes on the gold, however finely reduced, provided that the metallic particles be not coated with a protective covering, and if the precaution has been taken not to pulverize or stamp the ore too fine when about to be submitted to those preliminary washings which precede the amalgamation, the amount of the precious metal lost may be reduced to a minimum. When about to be brought into actual contact with the mercury, the ore or schlich cannot be reduced too small, and hence the importance of actually pounding it, if possible, under the surface of the mercury.

From these considerations it will be readily seen that the process of amalgamation is not only applied with advantage in the working of auriferous veins or lodes, but that it may also be employed to procure a profitable return from the re-working of the tailings or refuse of the Australian or Californian gold-diggers.

To give an idea of what may be done with poor ores, when system and skill are brought to bear, it may be sufficient to state the average produce obtained from the stamped ores at Schemnitz, in Hungary, in 1842—recollecting that these had to be broken from the solid lodes at depths extending to 200 fathoms. The total quantity stamped in that year was above 40,000 tons, and the average of the useful metals extracted from 50 tons was: gold, 3 ounces; auriferous silver, derived from the separating processes, by buddles or tyes, &c., $3\frac{3}{4}$ pounds; lead, similarly obtained, $8\frac{1}{3}$ cwts.; the ratio of gold to the other materials being in this case as 1 part to 500,000. In the case of a particular mine, called Siglisberg, not producing lead with the stamped ores, the ratio of gold was only as 1 part to 760,000; of auriferous silver, 1 to 24,000. Now, it is interesting and instructive to compare with this economical extraction of minute quantities from poor ores by the process of amalgamation the produce of the manipulation by washing at the Siberian workings, where a common average of the sands worked to profit is half an ounce in 1 cwt., or fully double the amount last mentioned, and yet even the poorer ones of Hungary yield a remunerative return by amalgamation. It follows, that by the same process many auriferous sands in Siberia, as well as in other countries, which are at present neglected as being too poor for washing, might be advantageously worked.

Separation of Gold from Arsenical Pyrites.—An illustration of the importance of scientific knowledge in the working of gold mines is furnished by the application of Plattner's method for the separation of gold from arsenical pyrites, in consequence of which the mines of Reichenstein, in Silesia, which, as already stated, had been abandoned for more than five centuries, were reopened with advantage.

This process is now largely practised in California under the name of the "Chlorination" process, and consists in treating the roasted sulphurets with nascent chlorine, whereby all the precious metal is dissolved, and water having been added, the gold is subsequently deposited from this solution by means of protosulphate of iron. The headings from the buddle, after being tossed, &c., are introduced into a common furnace, and roasted in order to oxidize all the sulphur present in the ore. This roasting causes a considerable decrease in weight, a ton of crude sulphurets yielding about 1450 lbs. of roasted ore. This is introduced into impregnation vats formed of wood, and having an inside coating of pitch and tar; they are provided with false bottoms, generally of quartz pebbles, above which is laid a perforated earthenware plate. The ore, *slightly* damp, having been placed in these vats, the lids are fitted closely on and chlorine gas introduced under the false bottoms; this gas being produced in a leaden generator by the action of dilute sulphuric acid on a mixture of binoxide of manganese and common salt. This generator is represented in Fig. 5, Plate I. It contains an agitator of hard wood, and is closed by a cover resting in a water-joint, the whole being placed on a sand-bath. Prior to passing into the leaching vats any hydrochloric acid which may be present is removed by passing the gas through water. After remaining in the gas for forty hours the lids of the vats are removed, water is poured on the surface of the ore in order to dissolve out the gold chloride, and this is run finally, as a yellow solution, into the precipitating vats, which, in construction, are very similar to those used for impregnating. The gold is here deposited by the aid of a solution of protosulphate of iron, and after being allowed to settle over night the supernatant liquid is drawn off, and the gold treated with sulphuric acid and common salt in order to remove oxides and basic iron salts. The precipitate is finally filtered, dried in cast-iron retorts, and melted into ingots usually about 960 fine.

The general arrangement of chlorination works is shown in plan and elevation by Fig. 3, Plate I. A Bruckner's cylinder, in which the ore undergoes a preliminary roasting to remove precipitating agents, such as sulphur, antimony, and arsenic, is shown at I. The leaching vats are at A, the precipitating vats at B, trucks to remove spent ore at C, the gas-generator at D, and the waste tub, where the water runs through sawdust, at E.

Many other methods are adopted for extracting the precious metal from the tailings, &c., but the reader requiring further information must be referred to the larger treatises, such as "The Mining and Metallurgy of Gold and Silver," by Mr. J. A. Phillip, the "United States Statistics of Mines and Mining," &c.

Calvert's Chlorination Process.—The following process of extracting gold by means of nascent chlorine was devised by Crace Calvert, and is closely analogous to that of Plattner just described:—He found that if 2·2 parts of fine gold be added to 100 parts of pure sand, and placed in a bottle with a saturated solution of chlorine gas for twenty-four hours, only 0·5 part of gold is dissolved. If, instead of chlorine water, a mixture of chlorine water and hydrochloric acid be used, 0·6 is dissolved. If the mixture consist of sand, reduced gold, peroxide of manganese, and hydrochloric acid, 1·4 part gold is dissolved. It was thus abundantly proved that the fact of the chlorine being in its nascent state materially aided the solution of the gold, although even then there remained 0·8 part undissolved. After many experiments, he decided that the following is the best method for extracting on a commercial scale:—The finely-reduced auriferous quartz should be intimately mixed with about 1 per cent. of peroxide of manganese; and if common salt be used (which, together with sulphuric acid, may be substituted for the hydrochloric acid), this material should be added at the same time as the manganese, in the proportion of 3 parts of salt to 2 of manganese. The whole should then be introduced into closed vats, having false bottoms, upon which are laid small branches covered with straw, so as to prevent the reduced quartz from filling the holes in the false bottom. Hydrochloric (or sulphuric) acid is then added, and after standing for twelve hours, water should be poured in in sufficient quantity to fill the whole empty space below the false bottom. This liquid, after being pumped up several times, and allowed to percolate through the entire mass, is run off into vats, the gold being separated by means of a concentrated solution of protosulphate of iron. In cases where silver also is present, it is desirable to employ common salt and sulphuric acid, as by this means the chloride of silver formed is retained in solution by the excess of common salt. The silver is separated before proceeding to extract the gold and copper.

METALLURGICAL OPERATIONS.—Fusion.—When the gold is received from the *gold-washer*, in the shape of gold-dust, or when it has been separated from its ores by amalgamation or otherwise, it has now to be subjected to a series of metallurgical operations to obtain it in a state of perfect purity. The first of these is that of fusion with borax, and casting the metal into ingots, by which it is obtained in a convenient form, and freed at the same time from earthy and other impurities. For this purpose the gold dust from the washings, or the spongy gold obtained by amalgamation, is mixed with a little dried borax, and is introduced into a black-lead crucible, previously heated in a common melting furnace. After the fusion of the metal, a slag, consisting of the grosser impurities, accumulates on the surface; this must be thickened by the addition of a little bone-ash, and then skimmed off. The metal is now cast into ingots, by being poured into iron ingot-moulds, previously warmed and oiled by wiping the internal surface with a piece of tow dipped in sweet oil. It is an old practice, now discarded by some metallurgists as useless, to add to the metal, when thoroughly melted in the crucible, a small quantity of corrosive sublimate, the contents are then well stirred, and, in consequence of the volatilization of the sublimate, effervescence takes place. That this is attended with no injurious effect seems to have been fully established by a long experience; and that it may even be productive of benefit is probable, by bringing to the surface any extraneous matter which might be detached from the interior of the crucible, and so permitting its removal along with the slag. The crucibles which have been used in a series of such operations retain a portion of gold, which renders it important to preserve them, with a view to the subsequent extraction of the precious metal by smelting.

Smelting of Gold Ores.—Although the readiest method of extracting the gold from rich alluvial sands is by repeated washings, in the manner already described, and in the treatment of quartz rock, iron pyrites, and other auriferous minerals, the method involving the tedious operations of pounding, washing, and amalgamation is usually adopted; yet in the latter case the same object may be accomplished by direct *smelting*—a term technically applied to a process, or series of processes, by which a metal is extracted, by the agency of fire, from the substances with which it may be combined or mixed in nature. It is well known that by this method iron is extracted from its ore in the blast furnace, and some years ago a Russian gentleman, named Anossow, even proposed to smelt in this manner the auriferous sand of the Ural, alleging that a much larger quantity of gold could be so obtained than by the most skilfully conducted process of washing. His method consisted in smelting the sand with iron, the latter being employed simply as a vehicle to collect the gold, or to perform, in its melted state, the same part as mercury in the processes already described. When the gold was obtained in this state of combination, the mass was exposed to the action of sulphuric acid, by which the iron was dissolved and the gold remained in the insoluble residue. From some experiments which were made at the Museum of Practical Geology in London, it was found that, if it were advantageous on the score of economy, cast-iron

might really be so applied; and that when it is melted with gold, an alloy seems to be formed, from which the greater part, if not the whole, of the gold may be extracted by again melting the alloy in contact with lead. With regard to Anossow's process, experiments were reported to have been made on the large scale, which had perfectly succeeded; but a strong proof of its want of success is the fact that it has never been practically adopted.

From the well-known infusibility of quartz, it is evident that the smelting of *gold-quartz* could not be effected by merely exposing it to the strongest heat of a blast-furnace, without the addition of a flux; for although the gold would be melted, it would remain in the quartz, and no separation of the precious metal would take place. Even supposing the quartz to be first reduced to powder, the gold is present in too small quantity to separate from the infusible mass, and sink to the bottom. It is therefore necessary to add some substance which, at a high temperature, shall combine with the quartz, and produce a fusible compound, in which case the gold, more especially if combined with some other heavy metal, will, in virtue of its high specific gravity, fall to the bottom of the vessel.

The best flux for silica is carbonate of soda, but this is too expensive to be employed on the large scale. Lime, therefore, aided by the addition of oxide of iron, is usually employed for this purpose. Lime alone, or lime and clay in certain proportions, will combine with quartz at a high temperature, and produce a fusible slag. Oxide of iron will also suffice. When practicable, it is desirable to obtain the oxide of iron by roasting auriferous pyrites, such as that found in California or the Tyrol, for then the proportion of gold is increased by that contained in the pyrites. Whatever flux be employed, it is necessary, in the first place, to reduce the quartz to a comparatively fine state of division, otherwise a considerable loss of time and waste of fuel would be incurred in effecting the perfect combination necessary to insure the complete separation of the gold. Even in smelting, therefore, the crushing or pulverizing process is not dispensed with. Assuming that lime and oxide of iron are the fluxes employed, and supposing the pulverized ore to have been partly concentrated by washing, these substances are mixed in about equal proportions, and raised to a white heat in a blast or reverberatory furnace. When oxide of iron is employed as the flux, the reverberatory furnace is to be preferred, because in the blast-furnace a considerable portion of the oxide would be reduced, and a corresponding quantity of metallic iron liberated, long before the mixture attained the degree of heat requisite for the combination of the silica with the oxide.

The product of the combination is a fusible *slag* or glassy substance, through which the gold, also in a melted state, tends to sink to the bottom of the furnace. But as the portion of this metal present even in a large quantity of ore is very small, compared with the bulk of the materials through which it is diffused, it would be difficult to collect it *per se*, without very serious loss, in a crucible, and still more so in a furnace, whether reverberatory or blast. The operation is therefore materially assisted by adding another metal which shall alloy with and absorb the whole of the gold, and from which the latter can afterwards be easily separated—some metal, in short, which shall serve the same purpose at a high heat as mercury serves at the ordinary temperature. Of all metals, lead is found to be the best adapted for this purpose, not only on account of its readily combining with the gold in a melted state, but also as offering peculiar facilities for its subsequent separation from that metal. Lead has, therefore, been uniformly employed in the processes hitherto adopted on a large scale for smelting gold ores. The lead may be added to the mixture of ore and flux, either in the metallic state, or in one or other of its combinations, from which the metal may be set free. The materials most commonly employed to furnish the lead are litharge and galena—the former the protoxide, and the latter the native sulphide of that metal—although the rich slags obtained both from the smelting furnace and ore-hearth are also occasionally used. When litharge is chosen as the medium for the introduction of lead, it must be mixed with charcoal, small coal, or coke-dust, in order to determine the reduction of the necessary quantity of lead to the metallic state; but when galena is used, it is mixed with scrap-iron, which combines with the sulphur, setting the lead free. The lead-slag which comes from the ore-hearth or the reverberatory furnace is generally the most convenient and least expensive material, as it contains a considerable percentage of lead, and is readily prepared for use by grinding to powder under the edge-roll, and mixing with charcoal or other carbonaceous matter. In this case, also, it is important to add some scrap-iron to combine with any sulphur which may be present in the slag. Whichever of these substances be employed, the lead evolved, under the conditions mentioned, percolates through the mass, and subsiding by virtue of its high specific gravity to the bottom of the furnace, carries along with it any particles of the precious metal it may meet with in its course. The lead is afterwards separated by *cupellation*—a process to be explained shortly.

Smelting with Iron Pyrites.—Instead of directly employing lead as the means of concentrating the gold ores, a method has been practised in Hungary in which iron pyrites, generally itself containing a small quantity of gold, is used with economical effect for the same purpose. When this mineral is heated to a certain temperature without access of air, it loses half of its sulphur, and becomes converted into a fusible sulphide of iron, such as is produced by bringing a roll of sulphur in contact with a bar of iron raised to a white heat. Let it be assumed, therefore, that this ore consists of a mixture of auriferous iron pyrites and quartz, and is mixed with the appropriate flux for the quartz, as already described, and exposed to the requisite heat; a slag will be formed, and the sulphide of iron

will unite with the greater portion of the gold present, forming a heavy regulus, which will subside to the bottom. The stratum of sulphide of iron thus formed beneath the surface of the slag and scoriæ produced by the fusion of the earthy and siliceous gangue, is technically termed a *matt*. If this matt, containing the gold, be now roasted, or *oxidized by heating it with free access of air*, whereby it is deprived of a further portion of its sulphur, and the product be mixed with a fresh quantity of crude auriferous pyrites, and smelted again, a second matt will be obtained, which will contain the gold from the first and second charges of the auriferous ore. This process may be repeated a third, fourth, or any number of times, until the precious metal has been sufficiently concentrated in the substratum of sulphide of iron to admit of its profitable extraction. The last matt, containing the whole of the gold which has accumulated from the successive charges, and brought, therefore, to any required richness, is then fused with metallic lead, litharge, or with a mixture of galena and metallic iron. The gold is abandoned to the liberated lead, from the top of which the impoverished sulphide may be readily skimmed off.

By this process the gold is obtained in a more concentrated form, or mixed with a smaller proportion of lead, than when the latter is used directly as a means of separating and collecting it from the smelted ore. Still, as the lead must be used for its final separation from the ore in all cases—even when the gold has been concentrated by washing and amalgamation—the employment of the iron pyrites in the manner above described is only attended with advantage when it constitutes part of the ore itself, or when it can be readily and cheaply procured in sufficient abundance. When it forms a principal ingredient in the ore, it is manifestly highly advantageous, in point of economy, to employ it as a vehicle for the concentration of the precious metal, while it contributes at the same time to increase the amount of the product.

Longmaid's Smelting Process.—In 1852 a patent was secured for another smelting process, invented by Mr. LONGMAID, which consists in separating the gold from the quartz or siliceous ore by introducing plates of wrought iron into the melted mass. The quartz is first crushed to a fine powder, and fluxed with a mixture of lime and oxide of iron, as usual. Into the fused mass thus obtained plates of wrought iron are from time to time introduced, and when withdrawn their surface is found to be coated with a film of gold. The plates are then plunged into a vessel of melted lead, which dissolves off the precious metal, and afterwards again put into the furnace. This process is constantly repeated till the whole of the gold is extracted from the ore; and it is said to be thus obtained both more economically and in greater proportion than by the usual process of washing and amalgamation. The gold is then extracted from this auriferous lead by cupellation, a process now to be described.

CUPELLATION.—The next metallurgical operation is the extraction of the gold from the lead, and this has been performed from the most remote antiquity by a process termed *Cupellation*. This process, which is very simple in principle, is at the same time one of the most elegant chemical operations ever invented. It depends on the circumstance that when silver and gold are exposed in a state of fusion to the action of the air or oxygen, they neither give off perceptible vapours nor are sensibly oxidized—they remain, in short, unaffected; whereas, under similar circumstances, lead and almost all the other metals are oxidized with greater or less rapidity. There is also an important peculiarity connected with lead, which renders it the only metal, except bismuth, applicable to the process of cupellation. This peculiarity consists in the circumstance that the oxide of lead, known as litharge, is fusible at a bright red heat, and in this state absorbs any other metallic oxide with which it may happen to be in contact, but which, without the influence of the oxide of lead, would remain uninfluenced by the heat. For example, if copper be present as an oxide, it is taken up by the melted oxide of lead; and if the latter can be separated from the gold and silver, the oxide of copper will be expelled along with it.

This separation may be effected in various ways, but particularly by means of bone-ash, which possesses the peculiar property of absorbing the melted litharge even when mixed with a certain proportion of other oxides, whereas it remains impermeable to the unoxidizable metals. Hence, if a vessel be formed of pounded and compressed bone-ash, and into this vessel a mass be introduced, consisting of a mixture of litharge or oxide of lead, copper or oxide of copper, and native gold, which always contains a certain proportion of silver; and if this mixture be exposed to a considerable heat, the whole will be reduced to a state of fusion; the oxide of lead will dissolve the oxide of copper, and both will be absorbed by the bone-ash, while the mixture of gold and silver will remain in the vessel, melted, but otherwise unaffected. Hence it follows that gold or silver, or a mixture of the two, may readily be deprived of copper or any other oxidizable metals by cupelling with oxide of lead. For this purpose it is not necessary to employ the oxide itself in the first instance. When metallic lead is heated to a temperature above its melting point, it rapidly combines with the oxygen of the air, the product being in the first place yellow oxide of lead, which appears as a scum on the surface; and when the temperature is raised to about bright redness, this oxide is converted into litharge or the fusible oxide, which immediately melts. Pure copper requires no less than sixteen or seventeen times its weight of lead to absorb it in the manner above mentioned.

A vessel of bone-ash, formed for this purpose, is termed a *cupel* or *test*; and in using such vessels for *assaying*, the absorptive power of the cupel is the only agency employed to separate the gold from the lead and other oxidizable metals, as will be explained afterwards. It is otherwise in cupellation on the large scale; in this case the cupel is soon saturated,

and the greater part of the litharge is expelled by a different method.

The English method of cupellation or refining is as follows:—A piece of bar-iron, about half an inch thick and 4 inches deep, is bent into the form of an oval hoop, and the ends of the bar are welded together. The greater diameter of this hoop, which is destined to form the containing circumference of the cupel or test, may be about 4 feet, and its lesser 2 feet 6 inches; but the dimensions vary considerably according to circumstances. On the lower part of the hoop are fixed four or five flat bars of iron, arranged parallel to each other in the direction of the short diameter. The first of these is placed about 9 inches from one end of the oval, and the others at about equal distances between this bar and the other extremity. The hoop is then placed with the cross bars downwards upon a solid floor, and a quantity of pounded and sifted bone-ash is beaten firmly into it with a mallet or rammer until it is entirely filled, or the bone-ash is level with the upper edge of the hoop. The bone-ash employed for this purpose is mixed with about one-tenth, by measure, of fern ashes, or one-fortieth by weight of American pearl-ashes, and moistened sufficiently to become coherent by pressure. The fern or pearl-ash has the property of giving greater consistency to the bone-ash when heated. When the hoop or frame has been well filled with this mixture and solidly beaten down, the surface is carefully scooped out with a trowel all round the centre, so as to form a shallow concavity of about $2\frac{3}{4}$ inches in depth, leaving a wall of bone-ash all round, about 2 inches in thickness at the top and 3 inches at the bottom, except at one end, where a thickness of 13 inches is left; whilst the thickness of the sole itself is reduced to 1 inch above the upper surface of the iron cross-pieces. At that end of the test where the wall was left 13 inches thick, and which is termed the *breast*, a segment of the bone-ash contiguous to the hoop is removed.

This apparatus is represented in Figs. 25 and 26, of which the former is a plan, and the latter a longitudinal vertical section. In these drawings the letters A A denote the iron hoop; *a a*, the tranverse bars; E indicates the cavity in the bone-ash; B, the breast; and F, the space where the bone-ash is removed between the breast and the iron.

In cupels of more modern construction the bone-ash is not removed from the part F, as the litharge is found to come into contact with the iron ring, on which it exerts a powerfully corroding action, when such an arrangement is adopted. In place of this, however, a round hole is cut in the centre of the breast near F, to which channels are cut similar to those shortly to be described.

When fully prepared, the test is allowed to dry, and is then placed in a furnace, constructed in all respects like a common reverberatory, except that a space is left open in the bed of the furnace to receive the test, and that the width of the arch is much reduced. The test, in fact, forms the bed of the furnace, in which it is adjusted with the long diameter transversely. It is supported in its place by an iron ring built into the masonry, or by iron bars placed underneath, between the two walls of the furnace. The fire-place of a cupelling furnace is usually about 2 feet in breadth, and 2 feet 6 inches in length. This is separated from the body or bed of the furnace by a fire-bridge 18 inches in breadth, so as to allow the flame and heated air to pass directly over the surface of the cupel, from whence it escapes through separate flues into a high chimney. At the side of the furnace opposite to the breast of the cupel the nozzle of a pair of large double bellows, or a fan-blast, is introduced.

When the cupel is inserted and the furnace lighted, the heat must be applied in the first place with much caution; for the test, if exposed suddenly to a high temperature before it has become sufficiently dry, is liable to split and fall to pieces. In the meantime the lead containing the gold and silver, and which, from this circumstance, is termed *rich lead*, is

Fig. 25.

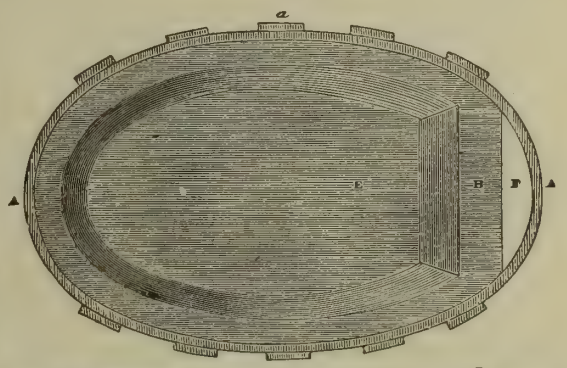




Fig. 26.

brought to a state of fusion in a cast-iron pot, set in brickwork at the side of the furnace; and when the test has been cautiously raised to a cherry-red heat, the rich lead is laded into it till nearly full. Oxidation now proceeds rapidly. At first the lead becomes covered on the surface with a yellow or grayish dross; but on further raising the heat, the surface of the bath "uncovers," and a film of melted litharge begins to appear. Part of this litharge sinks into the bone-ash of the test, which it soon saturates. The blowing apparatus at the back of the test is now set in motion, and forces the litharge as it forms forward to the breast, B, across the surface of which a channel is cut, through which the litharge begins to flow, and runs over at the end through the vacant space, F, into a movable iron pot, placed on the floor for its reception. The current of air introduced at the back of the cupel not only assists in clearing away the litharge, but supplies the amount of oxygen necessary for its rapid formation. In proportion as the litharge flows away, more of the melted lead is

gradually supplied to the test, which is done by lading it into a channel from the pot outside the furnace.

After a certain period, the channel first formed in the breast, B, becomes much corroded; it must then be stopped, and a second and third channel successively formed for the same purpose. In this manner the operation may be continued until 6 or 8 tons of the rich lead have been refined on the same test. Sometimes, however, two tests are employed, the first to concentrate the lead, and the second to separate it entirely from the precious metals. In this case, when the lead has been so far concentrated in the former, that the whole of the gold and silver contained in the alloy may remain in combination with only 2 or 3 cwt. of that metal, a hole is made through the bone-ash of which the bottom is composed, and the concentrated lead is received into a pot which is placed below. The tapping-hole is then closed with a pellet of moistened bone-ash, and a fresh charge of the original rich lead is concentrated in the same manner. When a sufficient amount of concentrated lead is thus accumulated to yield, as ascertained by assaying a small portion, from 1000 to 2000 ozs. of the precious metals, the whole is again melted down, and submitted to a second cupellation in another test, in which the operation of refining is completed.

Towards the conclusion of the operation some striking appearances are often presented. If the gold present is mixed with a considerable amount of silver, the surface of the mass, as it cools, is suddenly thrown into agitation; cones, or little craters, sometimes several inches in height, are thrown up, from which oxygen gas escapes with violence, projecting particles of silver with considerable force. This phenomenon is termed *spitting*, or sometimes *vegetation*, from the beautiful arborescent forms which are presented; and arises from the circumstance that metallic silver, when melted, has the property of absorbing or occluding six times its own volume of oxygen, which is ejected with violence at the moment of solidification. For reasons especially connected with the final process of *parting*, and which will be afterwards explained, there is almost always introduced into the alloy, before cupellation, a comparatively large amount of silver, so that the phenomena above described are uniformly observed at the conclusion of that process. Moreover in the cupel, the presence of a considerable proportion of silver is important, for the purpose of diluting the gold, and so diminishing the chance of loss.

After the cupelling, the test, with its cake of alloy of gold and silver, is withdrawn from the furnace; the metallic mass is removed and cleaned from external impurities; and the bone-ash, saturated with litharge, and any other oxide that may be present, is knocked out and preserved for subsequent treatment, as it contains not only a considerable quantity of lead in a state of oxide, but also a small proportion of silver.

On the Continent, the process of refining is conducted without the use of a cupel, properly so called. No bone-ash is employed. The test, if it may be so termed, is the bed of the furnace itself, which consists of a kind of marl, firmly beaten down into a circular cavity, which slopes from the sides to the centre, and allowed to dry. The roof of the furnace, which consists of a flat dome of bricks, built in a strong circular hoop of bar-iron, is movable by means of a crane. Several tons of lead are introduced at once, and after the roof has been replaced, the blast is transmitted through one or more apertures in one side of the furnace; the whole mass of metal is then worked off continuously, without any addition, till the lead is removed, and the alloy of gold and silver is left approximately fine.

Parting.—The final operation of separating the silver from the gold is termed "parting," and is generally performed in this country by means of nitric acid, which dissolves the silver without attacking the gold. On the Continent the same effect is produced with hot sulphuric acid. In assaying operations, nitric acid is always employed, and therefore the precautions necessary to be observed in this case will be fully explained in connection with the subject of assaying. In the meantime, the process with sulphuric acid, as practised on the Continent, will be first detailed.

1. *By Sulphuric Acid.*—It is only of late years that the use of sulphuric acid for this purpose has been generally introduced on the Continent, in consequence of its now being manufactured so much cheaper than nitric acid, formerly the only acid employed. The operation is performed in a very simple manner, and if any copper has been left in the alloy, it is separated along with the silver. It is true that the copper should be entirely expelled by the process of cupellation; but, as this process is practised on the Continent, a considerable amount of that metal often remains in the mixture; and its presence is by no means injurious, but is rather useful, in the subsequent operation of parting with sulphuric acid. Moreover, if too much copper be present, a sulphate is produced, of which only a limited proportion will dissolve in the concentrated acid. The proportion of gold also must be less, as compared with the amount of silver, than when nitric acid is used. Experience has shown that the alloy should not contain more than one-twentieth part of copper; and that the proportion of the gold to the silver should not exceed one-fifth; whereas, with nitric acid, it is sufficient if the weight of the silver amount to about three times that of the gold.

When the silver is not already present in the required proportion, which is never the case with native gold, the requisite excess must be introduced; for when the amount of gold exceeds the proportions above stated, the particles of silver are so enveloped in that metal as to resist for a long time the action of the strongest nitric or sulphuric acid. In the process of assaying, the proportion of rather less than 3 parts of silver to 1 of gold is very closly adhered to, for reasons to be afterwards mentioned; but in operating on the large scale with sulphuric acid, the proportion of the gold to the silver may vary from one-fifth to one-tenth, without inconvenience; and

Dumas states that the operation may be conducted with profit when the ratio of the gold to the silver does not exceed 1 : 1000; and at the present day even half this amount can be extracted with profit.

The alloy being prepared in the requisite proportions, which is generally done by introducing the excess of silver before cupellation, is melted in a crucible, and granulated by pouring it into cold water. For 1 part of the granulated alloy, $3\frac{1}{2}$ parts of concentrated sulphuric acid are taken, and the mixture is put into a platinum vessel, which is then introduced into the furnace. The vessel should not be more than two-thirds filled, to guard against the effects of effervescence, which might throw out part of the liquid. It is then covered with a platinum hood, provided with a beak or tube for conveying the gases and vapours into a condensing apparatus. The capacity of the platinum retorts varies, and there is usually an assortment of different sizes, for treating alloys of different qualities, without the necessity of mixing them. After two or three hours' boiling, varying the time according to the size of the retorts, the silver, and any copper that may be present, are completely dissolved.

On the first application of sulphuric acid to this purpose, the operation was performed in iron retorts. Vessels of platinum were afterwards introduced, as this was considered to be the only metal which could perfectly resist the action of hot and concentrated sulphuric acid. Afterwards, however, the enormous expense required for a complete assortment of platinum retorts induced attempts to return to the use of iron, and successful experiments were made by M. Tocchi, which proved that iron retorts might be safely employed, but platinum is still in use in many establishments. It was found that the very concentration of the acid presents, of itself, an obstacle to the precipitation of the silver or copper by the iron, and, further, that the interior surface of the retort acquires a coating of silver, so that the iron and the liquid soon cease to be in contact. This point has not been sufficiently studied; but the fact has been placed beyond doubt that the operation succeeds very well in iron vessels, and accordingly, in many refining establishments, no others are employed.

It cannot fail to be observed that, assuming the proportions above given, the quantity of sulphuric acid is much greater than would be strictly necessary to convert the silver and copper into sulphates. Supposing the alloy to be as poor as possible in gold, theory would indicate the following quantities of acid as being sufficient for this purpose:—

	Parts.			Parts.		
Copper,	50	would	require	155	sulphuric	acid.
Silver,	949	"	"	861	"	"
Gold,	1	"	"	0	"	"
Alloy,	1000	"	"	1016	"	"

But as the amount of sulphuric acid employed is actually 3500 to 1000 of alloy, there is an excess of about 2500 of acid, intended to hold the sulphates, especially the sulphate of copper, in solution.

When the silver and copper are completely dissolved, the retorts are withdrawn from the fire, and the solution is left to cool, in order that the gold may settle to the bottom. The liquid is then decanted; the gold, which remains in the vessel, is carefully washed, and the water employed in this operation is added to the sulphate solution. Lastly, the purified gold is melted, and after being cast into ingots, is ready for commerce.

The acid liquor containing the sulphates is poured into a leaden boiler, containing water and copper shavings. Heat is applied, and the sulphate of silver is soon completely decomposed. The precipitated silver is collected and submitted to repeated washings, always adding the water to the contents of the boiler, to be treated in the next operation. Lastly, the silver is dried in a small iron pan, and is then melted in a crucible, to be cast into ingots.

The acid solution, which now contains only sulphate of copper, is evaporated in the lead boilers till it is fit to crystallize. It is then put into the crystallizing pans, and the mother waters are further evaporated, to obtain more crystals. This process is continued till the liquid becomes very concentrated, and consists almost entirely of sulphuric acid. In this state it is termed "black acid," on account of its colour, which is due, in great part, to organic matters, dust, and other impurities, which fall in it during the evaporation in the crystallizing pans. The black acids may either be employed to repeat the same operation, or turned to useful account in different manufacturing processes, which do not require that the sulphuric acid should be pure and highly concentrated.

2. *By Nitric Acid.*—The operation of parting is performed with nitric acid in much the same way; but all the details of the process with this acid will be minutely explained in connection with the subject of assaying, for which it is uniformly used.

3. *By Fusion with Sulphur.*—Another method of separating the gold from the silver, which is sometimes practised with alloys containing but very little gold, is by fusing the granulated alloy with three-tenths of its weight of sulphur; this combines with the silver, and forms a liquid sulphide, in which the finely-divided gold remains suspended. A small quantity of litharge is then added, which gives rise to the formation of sulphurous acid and sulphide of lead, and again separates a portion of the silver, and this combines with the gold, forming an alloy richer in the latter metal. This alloy, by its greater specific gravity, sinks to the bottom of the crucible, and after cooling, is separated by the hammer from the superincumbent mixture of sulphide of silver and lead. When this mixture, which is termed "plachmal," is fused with a small quantity of litharge, it yields silver, which for the most part still contains a little gold. The richer alloy which subsides to the bottom of the crucible, is treated repeatedly with sulphur in the same manner, till the proportion of gold is raised to one-fourth, and the final separation of the silver is usually effected with nitric or sulphuric acid. It will be observed that this

process is similar in principle to the method already described for concentrating auriferous pyrites.

4. *By Fusion with Sulphide of Antimony.*—In this case the alloy is mixed with 2 parts by weight of sulphide of antimony, and fused, with constant stirring, in a crucible, which should be previously glazed with borax. By this means sulphide of silver is formed, and the gold combines with the antimony, forming a stratum of alloy, and is afterwards separated from the antimony by simple ignition in the air, or by fusion with nitre. If the amount of silver in the original alloy exceeds one-third, a proportional quantity of sulphur must be added in the crucible. The sulphide of silver forming the upper stratum retains a small portion of gold, to separate which it is again twice fused with sulphide of antimony, and this is again removed by ignition or fusion with nitre. The same operations are repeated on the whole amount of antimonide of gold thus obtained, and the antimony is finally removed either by fusing the antimonide alone, while air is blown upon it, or by fusion with three times its weight of nitre. Sometimes it is melted into a mass by heating with three-fourths of its weight of borax, one-fourth of nitre, and one-fourth of glass.

5. *By Cementation.*—Another method, which is practised in America, consists in arranging the granulated alloy in alternate layers, with a mixture of 2 parts of brick-dust and 1 part of chloride of sodium in porous crucibles, which are exposed to a low red heat in a wood fire for a period varying from twenty-four to thirty-six hours. The aqueous vapour from the wood permeates the crucibles, and acts upon the salt in such a manner as to separate hydrochloric acid, which then forms chloride of silver with evolution of hydrogen. The chloride of silver, together with the chloride of sodium, sinks into the brick-dust, and the gold obtained after washing contains not more than 9 or 10 per cent. of silver.

In this case, without the brick-dust, the conversion of the silver into chloride would be only superficial, because the chloride first formed would protect the inner portions of the alloy from the action of the hydrochloric acid. But when the alloy is enveloped in brick-dust, the chloride of sodium is partly decomposed by the silica, yielding silicate of soda and hydrochloric acid; the latter converts the silver into chloride, which then fuses with the rest of the chloride of sodium, and this, sinking into the brick-dust, leaves a new surface of alloy exposed to the action of the acid.

The reader will observe that the three methods last mentioned are all more or less imperfect in their results, and that for the complete separation of the silver recourse must always be had to the action of sulphuric or nitric acid.

Refining of Brittle Gold.—F. B. Miller has recently proposed a method of refining gold by means of chlorine gas, which is peculiarly suitable for removing such metals as lead, arsenic, antimony, and bismuth, metals which, even if only forming the $\frac{1}{1920}$th part of the whole mass, render the metal brittle, and totally unfit for coinage and the arts. This process consists in passing the gas through the metal while in a molten state for about four or five minutes. The above metals are thus converted into volatile chlorides, which escape, and should there be any silver present it is converted into chloride of silver, which floats on the surface of the metal. In order to avoid loss of silver an earthenware crucible should be employed, which has been previously dipped in a solution of borax, borax should also be introduced into the crucible together with the gold.

Fig. 27 shows the arrangement adopted by W. C Roberts in the Royal Mint for refining brittle gold by the process above described, where operations have recently been carried on on an extensive scale. The chlorine is generated in an iron vessel having a capacity of 8 gallons, and situated behind the flue. From it the gas is led by means of a tobacco pipe underneath the surface of the molten metal, the pipe passing through the cover of the crucible, which, of course, should not be luted.

Alloys of Gold.—Standard Gold.—By the preceding series of mechanical, metallurgical, and chemical operations, gold may be brought to a state of nearly absolute purity; but in this state it is too soft to be employed with advantage in the arts, or for the purposes of the coinage. Gold is therefore almost always alloyed with a greater or less proportion of some other metal, except when in the shape of the finest gold leaf, which requires for its proper manufacture a very high degree of purity, because, although it readily forms alloys with most of the other metals, its malleability is greatly impaired by their presence even in small quantities. With some metals this effect is very remarkable; even $\frac{1}{2000}$th part of antimony, bismuth, tin, or lead, will render the gold quite brittle. At the same time, as a natural consequence, its hardness and sonorousness are increased.

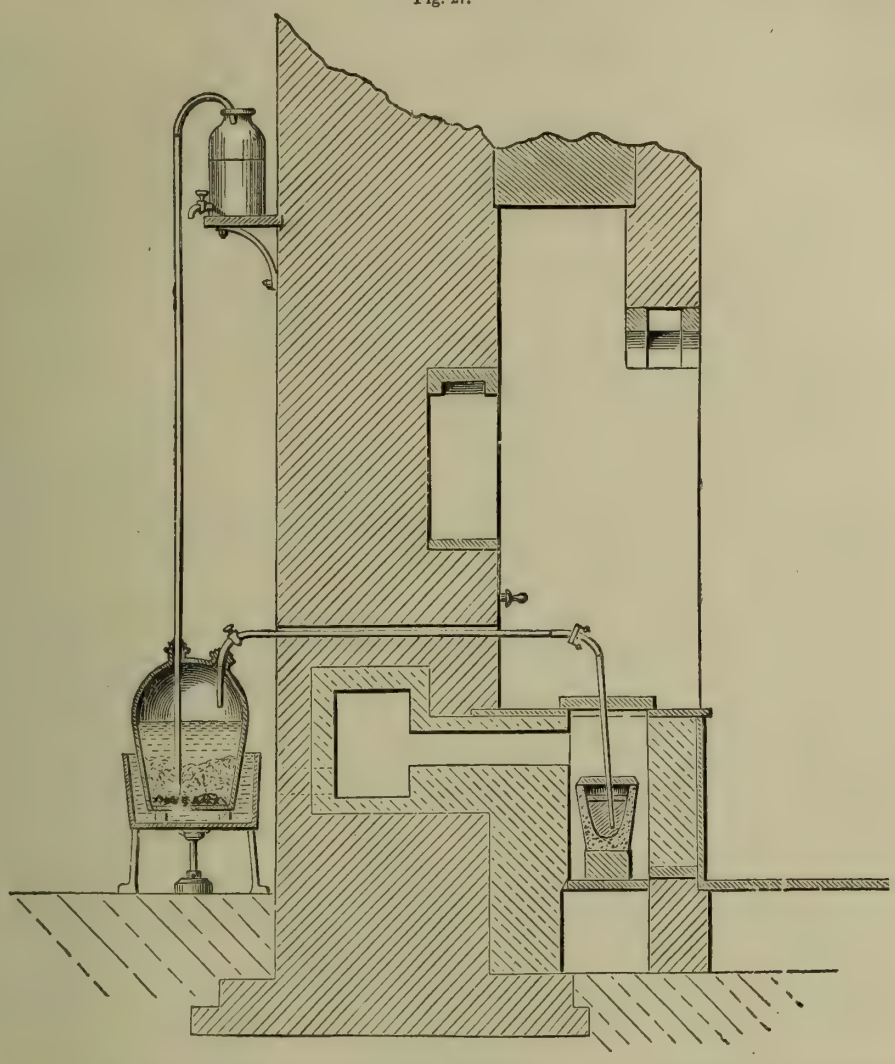
It is possible to obtain alloys of gold with nearly all the metals, but they are unimportant in the arts with the exception of those with silver and copper, metals which tend to increase its hardness and durability; these metals are also used by jewellers to give the gold different tints, according to the proportions employed. They are, it will be observed, the metals with which it is chiefly combined in the native state, although it is occasionally found associated with iron, platinum, tellurium, and other metals. The alloy or amalgam of gold and mercury is very important, and reference has already been frequently made to it.

Gold may be alloyed with silver in almost all proportions, and by its combination with this metal it becomes not only harder and more sonorous, but also more fusible. As the proportion of silver increases, the colour quickly passes through pale greenish-yellow into white. The malleability of gold is less diminished by silver than by any other metal. The maximum of hardness is found in the alloy containing 2 parts of gold to 1 of silver. The *green gold* of jewellers contains 30 per cent. of silver.

The most useful alloy of gold is that which is formed with copper, the alloy used for coinage.

The addition of copper renders gold redder, harder, and more fusible. The maximum of hardness is exhibited by an alloy of 7 parts gold and 1 of copper. English standard gold contains 8·33 per cent. of

Fig. 27.



copper, or 1 part of this metal to 11 parts of gold. In France the standard gold contains 10 per cent. of copper. Gold contracts in the act of solidifying from a state of fusion, and consequently cannot be made to receive sharp impressions by casting it in moulds. Coins are, therefore, stamped with a die, and plate is either stamped or embossed, and afterwards chased and carved, if necessary, by cutting tools.

Valuation of Gold Alloys.—In this country the standard of the alloys of gold is calculated in fractions of unity expressed in carats. Perfectly pure gold is taken as unity, and this is assumed to consist of 24 fractional parts termed *carats*, each of which is divided into 4 imaginary grains, and these are again subdivided into eighths and "excess grains," so called in contradistinction to the primary divisions of a carat or "carat grains." One carat grain contains 60 excess grains; thus the divisions of the original weight or "Assay Pound" taken will be as represented in the following table:—

Assay Pound.	Carat.	Carat Grain.	Eighth.	Excess Grains.	Decimal Equivalent.
				1	Per Cent. ·017
			1	7·5	·130
		1	8	60	1·042
	1	4	32	240	4·167
1	24	96	768	5760	100 000

From the above the meaning of the term "excess grain" will at once be evident. It is the $\frac{1}{5760}$th part of the weight of metal taken for assay, this ratio being the same as that borne by a troy grain to a troy pound. For accurately reporting the amount contained in a given alloy, it is necessary to use subdivisions less than eighths. "Excess grains" are therefore employed, and their number is the same

as the number of actual grains of gold contained in a troy pound in excess of the amount represented by the report in carats, grains, and eighths.

It has been stated above that the standard alloy of the English gold coinage contains 11 parts of gold to 1 of copper, or, in other words, 22 parts of gold to 2 of copper; it is therefore said to be 22 carats fine. When assays are reported on this system, which is called the "trade" system, the actual amount of gold is not given; but the metal is described as so much better or worse than standard, to indicate which the letter B or W is prefixed. Thus, suppose an assay be given as

	Cts.	Grs.	Eighths.		Excess grains.
B	1	3	5	+	3·5,

it means that it actually contains 23 cts. 3 grs. 5 eighths and 3·5 excess grains in the total amount of 24 carats. The percentage composition of such an alloy would be 99·66 per cent. of pure gold and 0·33 per cent. of alloying metal (generally copper or silver).

Although the above method of reporting is clumsy and complicated, it is found to be very convenient when masses of metal varying in weight and composition have to be alloyed and mixed, so as to bring all to a definite composition, and is on this account still partially retained in the Mint. It has, however, been very generally replaced by the following more uniform system, in which decimal fractions are employed, and which has the advantage of being equally applicable to gold and silver. Upon this system fine gold or silver is termed 1000·0, and the report upon any sample of alloy simply indicates the number of parts of pure gold or silver in 1000 which the sample contains. Unfortunately the English standard does not admit of expressing the amount of gold in a terminating decimal, the nearest convenient fraction being 916·66 of gold in 1000 of alloy. In France the standard is conveniently expressed by 900 of gold to 100 of copper. This decimal standard admits of the ready comparison of gold alloys with other chemical compounds, because in analytical investigations the results are always sought with reference to the percentage or centesimal composition of the substance under examination; but when the composition is given in carats, grains, &c., in the case of gold, or in ounces, pennyweights, &c., in the case of silver (a method which will be found described under Silver), it is necessary that these should be converted before such comparisons can be made. The following table, which gives the values of the divisions used in the old method expressed in decimal fractions, will be found convenient for effecting any required conversion in the case of gold. As an example of its use, suppose it be required to convert the above trade report into its equivalent on the decimal system—

23 carats are equivalent to....	958·22	thousandths.
3 carat grains,.....	31·25	"
5 eighths,.....	6·51	"
3·5 excess grains,.....	0·61	"
	996·59	

Carats.	Decimal Equivalent.
1	41·667
2	83·333
3	125·000
4	166 667
5	208·333
6	250·000
7	291·667
8	333·333
9	375·000
10	416·667
11	458 222
12	500·000
13	541·667
14	583·333
15	625·000
16	666 667
17	708·333
18	750·000
19	791·667
20	833·333
21	875 000
22	916·667
23	958·222
24	1000·000

Carat Grains.	Decimal Equivalent.
1	10 417
2	20·833
3	31·250
4	41·667

Eighths.	Decimal Equivalent.
1	1·302
2	2·604
3	3·906
4	5·208
5	6·510
6	7·812
7	9·115
8	10·417

Excess Grains.	Decimal Equivalent.
1	0·174
2	0·347
3	0·521
4	0 694
5	0·868
6	1·042
7	1·215
7 5	1·302

Coinage—History.—Although it is not proposed here to give an elaborate history of coinage, yet it may not be uninteresting briefly to sketch the leading facts in the history of money from the earliest times of which any records exist, and to give some account of the coinage of Great Britain, which will be followed by a description of the manufacture of money as at present carried on in the Royal Mint.

The use of coined money is by no means so ancient as might be supposed, unless it be true, as stated, that in the collection of Chinese coins in the Paris Mint there is one which dates as far back as 1700 B.C.; for the invention of true coins appears to have taken place about the seventh or eighth century B.C. Before this time payments were made by means of pieces of silver or gold, which are not supposed to have borne any impression whatever, or to have been of any definite weight. The weight used as an unit seems to have been such that it represented the value of some property frequently bought or sold. Thus in the book of Job the word "kesitah," meaning a "lamb," is translated "a piece of money." Doubtless this amount of silver represented the value of a lamb; and, indeed, in an ancient Egyptian painting we have a representation of ring money being weighed against weights made in the form of a lamb. Personal ornaments were also frequently made of a definite weight, in order that they might be used as a medium of exchange, and are called "jewel-money." The "ring money" mentioned above was made of gold or silver wire bent in a circle (about 2 or 3 inches in diameter); but the ends were not united, in order that they might be joined into a continuous chain.

The honour of having first invented coined money passing by tale and not by weight has been given to various nations of antiquity; it seems most probable, however, that the Greeks were the real inventors, as theirs is the only coinage in which a gradual progress can be traced. As Homer mentions that an ox was exchanged for a "bar of brass" of a

certain size, it is evident that coins did not exist in his day; and, on the other hand, since reference is made to them in the laws of LYCURGUS, we are assured of their employment at that date. Thus their invention is fixed between these two dates, that is, B.C. 950 and B.C. 820, or as nearly as we can tell at about 880 B.C. This money consisted, so far as we have any records, of "spikes," or small brass or iron obelisks, which were of such a size that the hand could just manage to grasp six at once. From this fact were derived the names *obolus* (a spike) and *drachma* (a handful) for two Greek coins in use long afterwards, one of which was worth six of the other.

It is interesting to note that in the earliest gold coinage ever issued—that of Lydia, in Asia Minor—the same ratio existed between it and the smaller silver coins as at the present day our sovereign bears to the shilling.

While to the Lydians is generally ascribed the first introduction of gold coins, it is generally supposed that the invention of silver money rightly belongs to the inhabitants of the Island of Œgina, of whose coinage specimens exist similar to the earliest Greek coins, bearing on the reverse simply the rude form of a punch mark, without any attempt at ornament.

In the earlier moneys the portraits borne always represented gods, or some animal considered to be typical of the town or state in which they were issued; and the introduction of human portraits on the coins did not take place till a comparatively recent period, when the art of coining had been brought to a high state of perfection. This was, however, at first only accomplished under a pretence of deification.

The metal adopted for the currency in different countries depended, as was natural, on the distribution of metals in those countries. Thus in Asia Minor the first money was of gold, and the metal is well known to have existed in the river Pactolus. Greece, on the other hand, possessing rich silver mines, its first coinage was of this metal. Italy, again, possessing as it did an immense supply of copper, its first money consisted of a kind of bronze, termed *æs*, in which copper is the principal ingredient. The Romans did not issue gold and silver coins till the years 207 B.C. and 281 B.C. respectively.

WILLIAM the Conqueror after the conquest replaced the old brass money of the Saxons by a coinage of silver, dividing the pound into twenty shillings and the shilling into twelve pence, a system which had already been introduced into France by CHARLEMAGNE in the eighth century. Gold coins were not introduced until the year 1257, when HENRY III. caused "gold pennies" to be struck of fine metal, although previously much *foreign* gold money was freely circulated in England. EDWARD III. introduced half a carat grain, or 0·5 per cent. of alloy, and the standard was gradually lowered to 22 cts., or 916·6 parts of fine gold in 1000 of alloy, a proportion first employed by HENRY VIII. in 1527; while once, in the year 1546, it was reduced by HENRY VIII. to 20 cts., or 833·5, the lowest gold standard ever known in England; but this was immediately replaced in the next reign by the old standards.

That introduced by EDWARD III. was 994·8, and was subsequently called "angel" gold, in contradistinction to the more modern standard 916·6, called "crown" gold, respectively from coins called "angels" and "crowns," issued of these two compositions. The two standards continued concurrently in use till about 1640, since which date the latter has alone been employed.

The alloys employed for the silver currency have undergone even more violent changes, principally, however, during the reigns of HENRY III. and his successor, when it fell as low as 333·3 parts in 1000, nevertheless the standard now in use is the one originally introduced by WILLIAM the Conqueror, and has been used uninterruptedly except at the times indicated.

The following table, which constitutes a portion of the 1st Schedule to the Coinage Act of 1870, gives the weight of all coins now legally current in both French and English measure, together with their least current weight, standard of fineness, and remedy

Denomination of Coin.	Standard Weight.		Least Current Weight.		Standard Fineness.	Remedy Allowance.		
						Weight Per Piece.		Millesimal Fineness.
	Imperial Weight. Grains.	Metric Weight. Grams.	Imperial Weight. Grains.	Metric Weight. Grams.		Imperial Grains.	Metric Grams.	
GOLD—								
Five pound,	616·37239	39·94028	612·50000	39·68935	$\frac{11}{12}$ fine gold, $\frac{1}{12}$ alloy; or millesimal fineness, 916·6	1·00000	0·06179	0·002
Two pound,	246·54895	15·97611	245·00000	15·87574		0·40000	0·02592	
Sovereign,	123·27447	7·98805	122·50000	7·93787		0·20000	0·01296	
Half-sovereign,	61·63723	3·99402	61·12500	3·96083		0·10000	0·00648	
SILVER—								
Crown,	436·36363	28·27590	—	—	$\frac{37}{40}$ fine silver, $\frac{3}{40}$ alloy; or millesimal fineness, 925.	1·81818	0·11781	0·004
Half-crown,	218·18181	14·13795	—	—		0·90909	0·05890	
Florin,	174·54545	11·31036	—	—		0·72727	0·04712	
Shilling,	87·27272	5·65518	—	—		0·36363	0·02356	
Sixpence,	43·63636	2·82759	—	—		0·18181	0·01178	
Fourpence,	29·09090	1·88506	—	—		0·12121	0·00785	
Threepence,	21·81818	1·41379	—	—		0·09090	0·00589	
Twopence,	14·54545	0·94253	—	—		0·06060	0·00392	
Penny,	7·27272	0·47126	—	—		0·03030	0·00196	
BRONZE—								
Penny,	145·83333	9·44984	—	—	Mixed metal, copper, tin, and zinc.	2·91666	0·18899	None.
Half-penny,	87·50000	5·66990	—	—		1·75000	0·11339	
Farthing,	43·75000	2·83495	—	—		0·87500	0·05669	

These data perhaps require some slight explanation.

Standard weight is the weight of a coin as prescribed by an Act of George III. Thus 20 lbs. of standard gold must contain 934 sovereigns and one ten shilling-piece; and every pound of standard silver shall be coined into sixty-six shillings.

Least current weight is the least weight at which the Bank can be *compelled* to accept a gold coin without making deduction for wear.

Remedy allowance is the latitude, or, in French, *tolerance* allowed to the Mint authorities within which the weight and fineness of coins may vary, as it would be impossible to produce the requisite number of coins *absolutely* correct both as regards weight and fineness.

Manufacture of Coins.—In describing the manner in which gold or silver, as received from the refiner, is converted into finished coin, we cannot do better than trace its progress from the time of the importation of the bullion in the form of ingots, to its being passed into circulation.

Importation.—Although the Mint authorities are legally compelled by the Coinage Act of 1870 to coin gold bullion free of charge, at the rate of £3 17*s.* 10½*d.* per standard ounce, by whomsoever imported, provided that it is not lower than standard fineness, the right is seldom taken advantage of by the public, and practically all the gold issued as coin is imported by the Bank of England. This liberty, however, does not extend to silver, for the money made of this metal is what is technically termed a "token" coinage, that is, it is not intrinsically worth the amount for which it passes current; an ounce of standard silver, which in the currency is worth 5*s.* 6*d.*, having an actual market value of about 4*s.* 10*d.*; this amount of course is liable to slight variations. Bronze money is also a "token" coinage. Thus it will be seen, that a profit of about 14 per cent. is derived from the coinage of silver money; this profit is called the "seignorage." It should be noticed, however, that whereas in the case of light gold the public are charged for the amount lost by wear, the Mint is always obliged to return new silver coin, piece for piece for worn coin, however much it may have lost in weight from this cause.

Gold and silver bullion are received into the Mint as (1) worn coin, (2) foreign coin, and (3) ingots. These latter are in the form of bricks slightly tapering downwards, and, in the case of gold, generally weigh about 200 ozs., and contain about 98 per cent. of fine metal. The silver ingots, which are purchased for the mint by a broker, usually weigh from 1000 to 2000 ozs., and are similar in fineness to those of gold. After being severally weighed, samples are cut off each ingot, and are then sent to be assayed (an operation which will be described subsequently) by the assayer of the Mint, who compares his results with those obtained by the importer's assayer. In case the two assays do not agree, a "retrial" is made, and should this confirm the first Mint assay, the importer is at liberty to sell on this result, or remove the metal from the Mint. The importer's assayer gives both a trade report and its decimal equivalent.

Melting.—The ingots then pass into the melting house, which is divided into two departments, devoted respectively to gold and silver. From the known weight of the metal and its composition it is easy to ascertain the amount of alloying metal (copper) which must be added in order to reduce it to the required standard of 916·6 and 925·0, in the cases of gold and silver respectively. Plumbago pots are used in both cases, those employed for gold being capable of holding about 1250 ozs., and those for silver from 2000 to 5000 ozs. of the standard alloy. The metal can, in the former case, be easily poured by hand, the pot being merely supported, while held in a pair of tongs, by a rope passing over a single pulley in the roof. With silver, however, in consequence of the larger weight operated upon, mechanical appliances have to be introduced. The pot, after being raised from the furnace by means of a common jib crane, is placed in an iron holder, which by means of wheel gearing can be gradually tilted, thus causing the metal to flow out. The moulds, about twenty-four in number, are fixed in a heavy iron frame, which runs on rails in such a manner as to bring them consecutively under the lip of the pot. In order to effect this the frame is provided with a longitudinal rack, which gears into a spur wheel on the fixed frame supporting the mechanism by means of which motion is given to the pot. Three men are required to work this apparatus. One turns a handle by which the tilting of the pot is effected; a second turns another handle in order to bring the moulds consecutively under the lip, at the same time holding back the charcoal (which always covers the surface of the metal, in order to prevent oxidation of the copper, whereby the alloy would be rendered too rich) to prevent fragments from passing into the moulds, while a third works two small racks, by which a slight motion may be given to the moulds to or from the pot, thus insuring a direct flow of the metal into the mould. In practice, however, it is found impossible to avoid spilling a considerable amount of metal when this apparatus is employed, the amount spilt in pouring gold, which is done by hand, being almost inappreciable. The bars, immediately on being cast, are removed from the moulds and cooled rapidly. The furnace in which the silver is melted is cylindrical in form, being about 30 inches deep and not quite 2 feet in diameter, 6 of these being connected with one central flue. They are provided with movable fire-bars and lids which slide over the top. Those employed for gold are similar in construction, but somewhat smaller. It is important to observe that, before pouring, the metal should always be stirred with an iron, fire-clay, or plumbago stirrer, as the gold (or silver) is liable to settle to the bottom of the pot, owing to its high specific gravity. During this operation, moreover, the fireman ascertains, from the viscosity of the molten metal, when it has attained the temperature which causes it, when moulded, to form the most workable bars. The bars are all of a

uniform length of about 24 inches, and the breadth and thickness vary with the different denominations of coins.

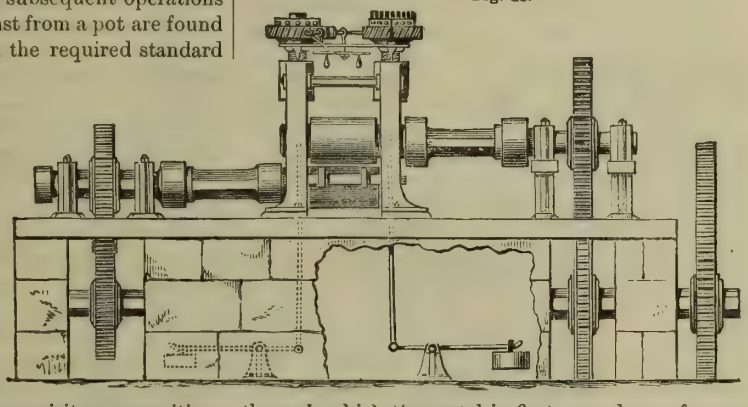
After being marked with letters indicating the day on which they were melted, and numbers to show the pot on that particular day, two bars are taken from each pot, and from the top of one (the extreme end having been previously removed by means of a cutting machine) and the bottom of the other, samples are removed for assay. The "legal remedy" or amount of variation permitted in fineness from the actual prescribed composition (916·66 in the case of gold, and 925·0 in that of silver) is for the former 2 parts in 1000, above or below, and for the latter 4 parts. Those employed in practice, however, are considerably less than above stated, in order both to insure against the possibility of any coins being issued "out of remedy," and to allow for those slight variations in composition which always take place during the subsequent operations of coining. When the bars cast from a pot are found to differ in composition from the required standard by more than this working remedy they are "stopped," and melted with such an amount of fine metal or copper as may be found by calculation to be necessary to convert them to the required standard.

In consequence of the contraction which the bars undergo on cooling the upper ends are hollow, and must be removed from all those which are ascertained to be of the requisite composition. This is done by means of an ordinary cutting machine in the melting-house, where they are also now trimmed and cleaned by means of a rotating cylindrical file, driven by steam power.

It may be well to explain that the above account describes the method actually practised in the English Mint, where modifications are from time to time introduced; moreover, in no continental mint are operations conducted in a precisely similar manner. Thus, it is frequently the practice to transfer the melted alloy from the crucibles to the moulds by means of iron ladles lined with clay. So general is this practice, that in the case of silver, in only one mint, that of Madrid, is the pot removed from the furnace as in England. Advantages are claimed for both systems, and Mr. Napier, reporting on the European mints, points out the following:—"The crucible left in the furnace will last two or three times longer; the metal is kept hot to the end; risk of accident from the breaking of the crucible is avoided, as well as the trouble of raking out the fire to remove the crucible, and the frequent resetting of it; a larger quantity can be melted at once, and the means employed for pouring are simpler. On the other side it may be urged, that direct pouring is quicker, and requires less labour, exposes the men less to the heat of the furnace, and empties the crucible entirely." In the British Mint the moulds are formed of a series of cast-iron bars having a T section; the alternate ones being reversed form a series of spaces thus—T⊥T⊥T⊥T⊥—of a size dependent on the width of flange. On the Continent, however, almost without exception, the moulds are recessed only on one portion, the covering portion being plain, a form which can be manufactured at less expense.

Rolling.—The bars having been thus prepared, are removed to the rolling room, where they are reduced in thickness to as nearly as possible that of the particular coin for which they have been prepared. In order to effect this it is necessary that they be passed through a series of rolling mills, in which the distances between the rolls gradually decrease from somewhat less than the primary thickness of the bar to that of the coin to be produced. The rollers

Fig. 28.



through which the metal is first passed are of heavy construction, as represented in the engraving, and need not be specially described, further than to state that the distance between the rollers, which are about 10 inches in diameter, is adjusted by means of two similar and carefully cut screws, the ends of which abut on the brasses of the upper rollers; motion is given to both simultaneously by worm-wheels fixed at their upper ends, these being caused to rotate equally by two similar worms fixed on one and the same axis. In these "breaking down" mills both rolls are driven by toothed gearing, a system, however, which gives rise to irregularities in the thickness of the "fillets," as the bars are called after being reduced to the required thickness. In some continental mints, in consequence, the upper roller is left free to be turned by the friction of the passing fillet, the power being communicated to the lower roll only.

Formerly when thick bars were employed (that is, 1 inch in thickness), the constant pressure caused the metal to become extremely hard, a circumstance which materially interfered with the final adjustment of the thickness, and had to be counteracted by annealing the fillets from time to time. This consisted in inclosing them (in the case of gold) in copper tubes made without solder, and which could, after the lids had been carefully luted on, be intro-

duced on an iron carriage into a furnace, where they were left for about twenty minutes. On being withdrawn, they were dipped into cold water. Silver fillets were also annealed, but resting on iron plates, the copper of the outer surface being thus oxidized. This oxide was subsequently removed by introducing the metal into hot sulphuric acid, as will presently be described. Bars only half or three-eighths of an inch in thickness are being gradually introduced for all denominations of coin; and it is found possible, when these are employed, to bring the fillets to the requisite thickness without annealing.

The last mill through which the metal is caused to pass is capable of more accurate adjustment than those employed for the preliminary rolling, and by its means the fillets are brought as nearly as possible to the required thickness of the coin.

When a fillet has passed through this gauging mill, the operator, in order to ascertain whether the distance between the rollers is correctly adjusted, cuts out a blank by means of a small hand screw press, provided with a ring-cutter and die suitable to the particular size of coin to be ultimately produced. This blank he weighs, and if its weight be within the working remedy the rollers are known to be the required distance apart. It is found, however, impossible in practice to roll a fillet uniform in thickness in its whole width; in consequence of the rollers yielding, the centre is perceptibly thicker than the edges, a fault which, if not corrected, would largely increase the amount of coin rejected on account of its being out of remedy as to weight. The apparatus employed in order to secure this uniformity is the draw-bench; and although several attempts have been made to complete the adjustment by means of rolling mills, no machine has given such good results. Before being operated upon by this instrument, one end of each of the fillets is introduced into a flatting mill, the object of which is to diminish its thickness to such an extent that it may be easily introduced between the two fixed edges of the draw-bench.

Adjusting Fillets.—There are in the Mint two benches, each capable of drawing two fillets at once, and being about 14 feet long by 2½ feet broad. Two endless chains pass along the whole length, and are supported on a drum at one end, while they are caused to travel along the bench by means of gearing driven by the steam engine, and situated at the opposite end, the loose half of each chain returning underneath the bench. Each link of the chains is provided with a short transverse bar, by means of which motion is given to the small carriage or "dog" after it has gripped the thin end of the fillet. The principal part of this apparatus by which the thickness is adjusted remains to be described. It consists of a strong rectangular frame of cast iron, having a vertical height of 20 inches and a width of 13 inches. In it are placed two solid blocks of metal, the lower of which is rigidly fixed by means of screws, and the upper is capable of a slight motion in a vertical plane by means of a very accurately cut screw, provided with a micrometer adjustment, while the distance between the two blocks can be adjusted by means of two screws with capstan heads, placed between them. There is a clear interval of 1½ inch between these blocks, while to the top of the lower and the base of the upper block small accurately-turned polished cylinders of fine steel, 3 inches long and three quarters of an inch in diameter, are rigidly fixed, touching the blocks along their whole length. These cylinders do not rotate, but form edges, between which the fillets are drawn by means of the dog; and this is so constructed that immediately on gripping the end of a fillet it is drawn towards the opposite end of the bench, at which the driving gear is situated. It will thus be seen that such an arrangement for diminishing the thickness differs essentially from the rolling mill, (1) in the fact that the faces between which the metal passes are fixed; and (2) the thickness of the blocks being very great in proportion to the width of the faces, the possibility of their bending is considerably diminished. The thickness of the fillets is tested in the same manner as it was on passing the gauging mill—by cutting out a blank of the size of the coin to be produced. Whereas, however, in the former case the working remedy was 0·5 grain for sovereign fillets, in the latter it is 0·2 grain.

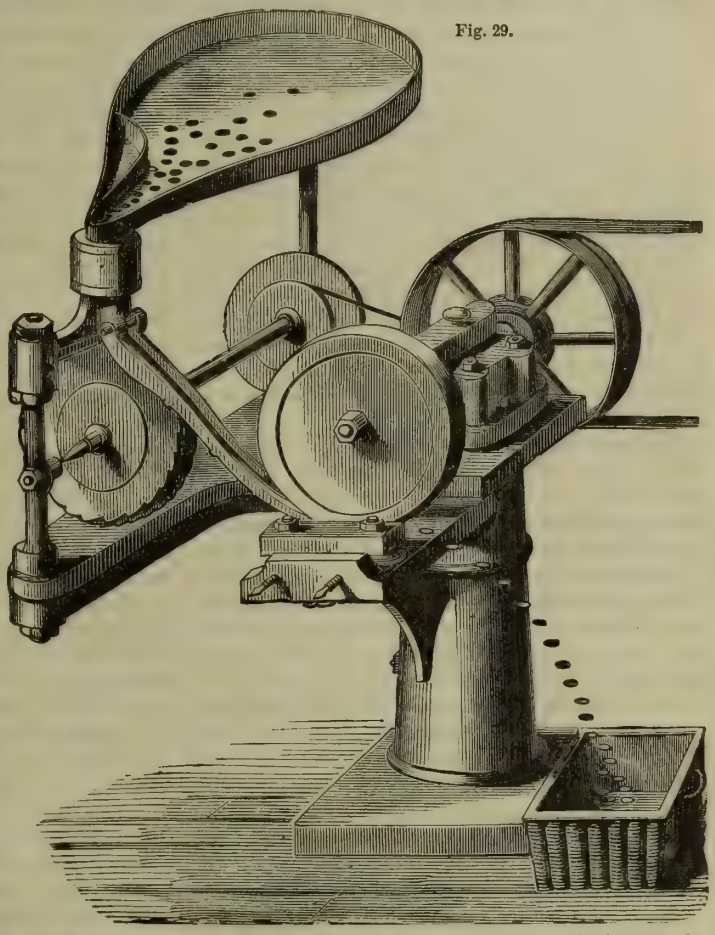
The heat produced by the friction between the steel faces and fillet is very great, and an abundant supply of oil must be kept up in order to diminish this as much as possible. All those fillets which are found to be of the correct thickness are cleaned, cut into lengths of about 15 inches, and passed into an adjoining room, where the next operation of cutting out blanks is conducted.

Cutting out Blanks.—The apparatus employed for this purpose in the British Mint is of ancient construction, and quite unfitted for the requirements of the present day; were it not that the Mint will, in all probability, shortly be removed from its present site and completely rearranged, the cutting out press would long ago have been replaced by machinery of a more convenient and less noisy description. The blanks are cut out by means of punches, the die, which is made of a size corresponding to that of the coins required, exactly fitting into a ring-cutter fixed below. There are twelve screw-presses arranged in a circle, and all driven by one large driving wheel situated overhead, and rotating in a horizontal plane, each press being separately assisted in its downward motion by a vacuum cylinder and piston situated beyond the walls of the press-room; this piston is raised during the ascent of the cutter, a motion which is brought about by the large driving wheel. The position of the fillet under the die is adjusted entirely by the eye, the object of course being to cut the blanks as close as possible, in order to diminish the amount of loss which must ensue on remelting the remainder of the fillet from which the discs have been removed, called *scissel*. In only one continental mint, that at Copenhagen, is machinery similar to that in our Mint employed; in all others the screw press has been replaced by the crank or eccentric press. It is generally driven by a strap to a pulley on

the crank-shaft, on which is also fixed a fly-wheel. Occasionally, in order that the fillet may be fed into the press rapidly and with precision, a movable stop is added, which takes its place in the last hole cut out, acting against the side nearest to the punch, and rising with the upward stroke to permit of the forward motion of the fillet. At the English and Belgian mints, heavy crank presses are employed for cutting two or three blanks at a time in bronze and sometimes silver. They are provided with a self-feeding arrangement, consisting of a pair of gripping rollers worked by a ratchet motion. As in the case of bronze the fillets are not passed through the drawbench, and are therefore thicker in the middle, it is found advisable, when cutting three blanks from the width, to make the central cutter somewhat smaller than the external ones, in order to secure greater uniformity in the weight of the coin. The scissel is usually tied up in bundles to be remelted.

Edge-Rolling or Marking.—In the Royal Mint *all* blanks, after a preliminary examination to remove such as are evidently imperfect, are passed through the edge-roller or compressor immediately on leaving the cutting-room, the object of which is to raise a rim round the edge to facilitate the formation of the relief at the circumference in the coining press, as also to protect the impressed surfaces of the coin from undue wear. It is represented in the annexed engraving, and consists of a circular steel plate which rotates on a horizontal axis, and having a circular groove on its face. Opposite to the lower portion of this groove is fixed a steel block, on the face of which is a corresponding groove, and the distance between the two can be accurately adjusted. The blanks are led to the space between these two by means of an inclined spout, at the upper end of which rotates, in a vertical plane, a wheel provided on its edge with slight saw-like indentations.

Fig. 29.



The metallic discs being led by means of a hopper to the top of this wheel, are distributed by its teeth, and pass down the guide with regular intervals between them to the pair of confronting grooves, and the distance between these being somewhat less than the diameter of the blank, its edge is pressed inwards, the thickness at the circumference being thereby increased. In many continental mints an inscription or ornamentation is impressed on the edge during this operation. In England, however, it is left perfectly smooth, the "milling" being produced in the subsequent operation of *coining*. It may be mentioned, that this instrument is capable of "compressing" blanks at the rate of about 700 per minute.

Annealing Blanks.—On leaving the edge-compressor the blanks are subjected to the process of annealing, by which they are rendered sufficiently soft to receive a well-defined impression of the die in coining. The methods adopted in the Royal Mint for annealing gold and silver coin have during the last few years undergone considerable modification. Formerly gold blanks were treated in closed iron tubes, and those of silver in open iron trays, but they are now all treated alike in copper tubes similar to those already described for annealing fillets. These tubes are nearly filled with the precious metal, and above is placed a layer of charcoal, the whole being then covered with a copper lid a number of them, containing in all about 3600 ounces of gold, having been placed on an iron carriage, are pushed into the furnace, where they remain for about twenty minutes. On their withdrawal the tubes are rapidly cooled by being plunged into water, by which means the oxidation which took place when they were allowed to cool slowly in the air is avoided. The blanks are now emptied into a copper colander, washed in cold water in order to remove the charcoal, and dried by agitation in a sieve with hot sawdust over a heated iron table.

This practice has only been adopted in the case of silver since the latter end of 1873; so that with this metal and gold the process of *pickling* or *blanching*, formerly considered important, is now almost entirely dispensed with. This included three distinct operations:—

(1) Heating the blanks and exposing afterwards to air, thus forming a film of oxide of copper on their surface.

(2) Removing this film by solution in dilute acid.

(3) Drying the blanks.

In the case of gold, as already mentioned, this oxidation of copper took place while the tubes were cooling in the air, while silver blanks were exposed from the commencement, being introduced into the furnace in open iron trays. The blanks, while in the colander, were cooled in water and dipped into a bath of dilute sulphuric acid (specific gravity, 1·021) where they remained for a few minutes, the oxide of copper being thus dissolved off and leaving a surface of pure gold or silver. They were then washed and dried in sawdust as above described. Blanching undoubtedly has the advantage of giving to the coins a better appearance when first issued from the Mint, but this thin superficial layer wears off much quicker than an equal thickness of the standard alloy would do: hence gold coins will continue a less time in circulation, being reduced below their least current weight. The question is, however, of but small importance to the public.

The annealing of copper blanks was formerly a very slow process, as the cast-iron tubes in which they were placed in the furnace were afterwards left to cool in the air by radiation, the blanks being then placed in dilute sulphuric acid for several hours. The method now adopted is a modification of the above, the tubes being, immediately on their withdrawal from the furnace, immersed in cold water and rapidly cooled; the blanching is performed as heretofore.

Coining.—The blanks having been thus prepared, nothing remains, as far as forming a completed coin is concerned, but to introduce them one by one into the coining press, whereby, at a single blow, not only the obverse and reverse impressions are given, but the crenated or "milled" edge is formed on those coins which require it. The presses employed in the British Mint are extremely antiquated, having been invented by Boulton, and made by the well-known firm of Boulton & Watt, and are of the form generally known as screw-presses. The blanks, having been arranged in a vertical hopper, are placed one by one in the press upon the lower die, which is fixed, by means of an automatic hand. Immediately upon the withdrawal of this hand a collar, slightly larger than the blank, rises round it in such a manner that, when the upper die is brought down with considerable force upon it, the metal is pressed against the inner rim of the collar, and as this is crenated, the edge of the now finished coin, on its removal, is "milled" in a corresponding manner. It is unnecessary further to describe this unhandy, noisy machine, which must ere long give place to some of the lever presses now almost universally employed on the Continent. The lever press is compact, and does its work in comparative silence. It is already in use in the majority of the continental mints, and at Copenhagen, where formerly presses similar to those in the Royal Mint were in use, the lever press has also been introduced. There are two forms in use, one invented by Thonnelier and the other by Uhlhorn. The power is communicated to a crank shaft, from which it is transmitted by a connecting rod to a lever and toggle joints, which actuate the arm carrying the upper die, by which means the pressure is given slowly and without a shock. The press, in addition to the advantages already mentioned, has the merit of being compact, simple in construction, and easily accessible for repair. It can be driven by a strap from a running shaft, and does not require a special foundation for its reception.

Weighing Individual Coins.—In nearly all the continental mints the blanks, immediately on being cut from the fillet, are weighed in order at once to reject those which would, if passed to the subsequent operations, produce illegal coins. In some mints those blanks which are too heavy are reduced in weight, the weighings necessary for this adjustment being performed by hand. In England and Spain, however, the individual weighing is only performed on each finished coin, and thus *all* the blanks are converted into coin; and although this entails the production of a certain number of finished coins which are ultimately rejected, it unquestionably affords a better guarantee for the maintenance of the legal weight of the coins. In this country the weighing is performed entirely by automatic machinery, and the apparatus employed for the purpose is the most remarkable and, except that employed in the Assay Offices, the most delicate in the Mint. The original form of this instrument was the invention of Cotton, but in those now in use several improvements have been adopted. No less than nineteen of these balances are now employed, each being capable of weighing twenty-two coins per minute to the hundredth part of a grain. The machine consists of a beam, on to one end of which is affixed a plate or table, and upon this the coin to be weighed is placed. The other end of the beam is provided with a scale pan containing a counterpoise weight corresponding to the coin in question, and a small stirrup or fork is affixed to the under surface of the pan. In certain positions of the beam this stirrup lifts up a small wire which represents the remedy weight of the coin. The action of the machine is as follows:—

A coin is placed upon the pan; if too heavy the counterpoise weight is raised together with the remedy wire; if too light, both the weight and remedy wire remain undisturbed; but if the coin is within the working remedy, the counterpoise weight is alone raised. The coin is then sent down a shoot, the position of the lower extremity of which over one of three slits is determined by the mechanism of the apparatus, and varies according as one or the other of the above conditions prevails. Those coins which are by this process ascertained to be of the

legal weight are each sounded on an iron block, in order to prevent such as are "dumb" or cracked from passing into circulation. Finally the finished coins are tied in bags, and, provided that such samples as are selected for assay are found to be of the legal composition, are issued to the public.

Jewellers' Gold.—The jeweller receives his gold in the form of ingots, which approach absolute purity, or 24 carats fine. He begins his operations by alloying it with copper or silver, or both, in certain calculated proportions, either to reduce it to the legal standard or to give it the particular colour required. The following are the three standards fixed by the statutes enacted in France on the subject:—1. *High standard gold*, consisting of 920 parts of pure gold in 1000 of alloy, which is equivalent to 22 cts. one-fourth ct. gr. and 4 ex. gr. This is the alloy usually employed by the French jewellers, and is nearly identical with the standard gold of the English coinage. 2. *French standard gold*, consisting of 840 parts of gold in 1000 of alloy, or 20 cts. five-eighth ct. gr. Sometimes it is reduced to only 20 carats. 3. *Common gold* is 750 parts in 1000, or 18 carats. The licence or *tolerance* allowed is 3 parts in 1000.

In England a greater number of standards is employed for jewellery, namely, 9, 12, 15, 18, and 22 carats; but the amount made of the second and fifth of these is extremely limited, and practically only the remaining three are in use.

In order that the gold may be easily worked, the alloy must be perfectly homogeneous, and the jeweller accordingly brings it to this state by repeated fusions. If the alloy has been badly made, and still exhibits a grainy appearance, with a liability to crack under the action of the hammer or between the laminating rollers, it must be again introduced into the crucible, and thoroughly fused with a mixture of borax and saltpetre.

In the "Dictionnaire des Arts et Manufactures," the colours most commonly required in articles of jewellery are stated to be composed as follows:—

Colours.	Composition.
Yellow gold,.....	Pure or fine gold, 1000.
Red gold, ...	Fine gold, 750; rose copper, 250.
Green gold,.....	Fine gold, 750; silver, 250.
Dead-leaf gold,...	Fine gold, 700; silver, 300.
Water-green gold,	Fine gold, 600; silver, 400.
White gold,.....	An alloy of gold and silver in which the latter predominates.
Blue gold,...	Fine gold, 750; iron, 250.

The last-mentioned alloy is somewhat difficult to prepare. It is obtained by introducing thick iron wire among the melted gold, and withdrawing the crucible from the fire as soon as the alloy is formed. When poured out and cooled, it should have no appearance of porosity. It is then forged, and formed into sheets or wires of different thicknesses.

Various shades of colour are likewise given by the jeweller to articles or ornaments of gold by the finishing process, which consists in exposing them to certain chemical reagents, to dissolve out a portion of the copper or silver from the surface, without attacking the gold. By this means the surface of the article is made to appear like pure gold, which it really is, while below the surface the quantity of copper or silver may be considerable. The liquor usually employed by goldsmiths and jewellers for this purpose is a mixture of 2 parts of nitrate of soda, 1 part of chloride of sodium, and 1 of Roman alum, in 3 or 4 parts of water. The trinkets or other articles are kept in this solution, at the boiling point, from fifteen to twenty-five minutes, according to the shade required. They are then taken out, washed in water, and after burnishing with bloodstone, the operation is finished. The pickle, or sauce as the liquor is termed, dissolves not only the copper or silver on the surface, but likewise a certain quantity of the gold itself. To recover the gold, the liquor is diluted with at least twice its bulk of boiling water, and a solution of very pure protosulphate of iron is poured into it. The precipitated gold is washed upon a filter, dried, and purified by fusing in a crucible, along with a mixture of equal parts of nitrate and biborate of soda. The other metals can likewise be recovered by very simple methods.

Gold-Beating.—The art of beating gold into thin leaves seems to have been known from a very remote period. The fact that the Hebrews were acquainted with it has been already stated; and from the circumstance that, on the coffins of the Theban mummies, specimens of leaf-gilding are met with, in which the gold is so thin as to resemble modern gilding, it may be inferred that the Egyptians had carried the art to a high degree of perfection. This art is distinctly referred to by Homer, and was practised extensively by the later Greeks, even to decorate the external sculpture of their temples and statues. Pliny states that after the destruction of Carthage the Romans began to gild the ceilings of their temples and palaces, and that luxury advanced on them so rapidly that in a little time even private and comparatively poor persons gilded the walls, vaults, and other parts of their dwellings. Horace's remark, that *neither ivory nor gilded arch figured in his house*, is familiar to the classical student. Pliny further states, that 1 oz. of gold was extended to 750 leaves, each 4 fingers square. Lucretius compared the Roman gold-leaf to a spider's web, and Martial described it as little other than a vapour; yet, according to Pliny's account, it must have been three times the thickness of the ordinary leaf-gold of the present time.

Experiments have been made to ascertain to what degree of thinness gold and silver could be reduced: it was found that 1 grain of gold was spread to the extent of 75 square inches, and the same weight of silver to the still more extraordinary dimensions of 98 square inches. Taking 1 cubic inch of gold to weigh 4900 grains, it will be found that the gold was the 367,500th part of an inch in thickness, or about 1200 times thinner than ordinary writing paper. Thus, if 367,500 leaves of gold were placed on one another they would constitute a pile only an inch high, while the same number of leaves of paper would form a pile half the height of the Monument of London. The same *weight* of silver,

though extended over a much larger surface, was thickest, owing to the difference in its specific gravity. In practice, the gold leaf is never extended beyond the $\frac{1}{280000}$th part of an inch in thickness.

The late Dr. Ure erroneously states, that the gold used in gold-beating ought to be of the finest standard. Alloy, he adds, hardens gold, and renders it less malleable; so that the fraudulent tradesman who should attempt to debase the gold would expose himself to much greater loss in the operation than he could derive profit from the alloy. From this statement it might be inferred that nothing but fine or perfectly pure gold is used by the gold-beater, whereas, in point of fact, it is alloyed in various ways, according to the colour required. Indeed, it is not uncommonly supposed, among the workmen employed in the business, that fine gold is incapable of being reduced to thin leaves; but this also is an error. It is simply objectionable for commercial purposes, on account of its greater cost, and also on account of the adhesion which takes place when one part of a leaf of fine gold touches another, thus causing a waste of labour by the leaves being spoiled. For work, however, which is to be exposed to the weather, fine gold is the best, being more durable, and not liable to tarnish or change colour.

A London gold-beater, E. S. Marshall, exhibited specimens of gold-leaf at the Great Exhibition of 1851, for which the prize medal was awarded to him. The specimens were twelve in number, and embraced a regular gradation in colour from red to nearly white—namely, red, pale red, extra deep, deep, orange, lemon, deep pale, pale, pale pale, deep party, party, and fine gold. The deeper colours were alloyed with from 12 to 16 grains of copper per oz., but no silver, since any admixture of this metal with so large a quantity of copper would considerably impair the malleability of the alloy; the medium colours contained from 12 to 20 grains of silver, with from 6 to 8 grains of copper to the oz.; and, lastly, the paler leaves contained from 2 to no less than 20 pennyweights of silver to the oz., but no copper, for the same reason that silver was omitted in the red or deep-coloured golds.

The process of gold-beating is purely a mechanical operation, but involving as it does one of the most important applications of this precious metal, it will be necessary to give a short account of it. The first operation is the *casting of the metal into ingots*. For this purpose the gold, either pure or alloyed, according to the colour desired, is melted in a crucible at a higher temperature than is simply necessary to fuse it, by which its malleability is improved. It is then poured into moulds previously heated and greased on the inside, and cast into flat oblong ingots, each about three-fourths of an inch wide, and weighing 2 ozs. The ingots, when taken from the moulds, are annealed in hot ashes, which cleanse them from grease and increase the malleability of the gold. When the ingot is cold, the French gold-beaters hammer it out to the thickness of one-sixth of an inch, and expose it at the same time to repeated annealings; but this operation, termed the *forging*, is omitted by the English gold-beaters. The next process is the *lamination*, which consists in repeatedly passing the ingot between two rollers of polished steel, gradually brought closer together, until it is formed into a riband of $1\frac{1}{2}$ inch in width, and 10 feet in length, to the oz. By this means the ingot is spread out to a surface of 960 square inches of the thickness of rather more than $\frac{1}{800}$ of an inch. The next operation is the *beating*, for which purpose the riband of gold, after being annealed or softened in the fire, is carefully divided with compasses and cut up into pieces 1 inch square, each weighing about 6 grains; about 160 of these are placed by means of wooden pliers between the leaves of a *cutch*, which formerly consisted of a packet of fine calf-skin vellum, but now it is usual to employ a tough paper manufactured in France. A case of strong parchment, open at both ends, is drawn over the cutch, and this is inclosed in a second similar case at right angles to the first, so as to cover the edges which the first had left exposed. The cutch is then beaten with a 17 lb. hammer, upon a smooth block of black marble, supported on a strong bench, and surrounded on three sides by a wooden ledge, while the front is left open, and has a leathern apron attached to it, to preserve any fragments of gold that may fall out of the packet. The hammer is short-handled, and is wielded by the workman with one hand, while with the other he occasionally turns the packet over, to distribute the force equally. The elasticity of the packet causes the hammer to rebound, and lightens the labour of the operator. At intervals the packet is taken up, and bent or rolled between the hands, to overcome any slight adhesion between the leaves and the interposed paper or vellum; or it is taken to pieces to examine the state of the gold, and to shift the central leaves to the outside, and *vice versâ*.

When the gold plates of 1 inch side are thus spread out into 4-inch squares, or to nearly the size of the leaves of the cutch, which generally requires about twenty minutes' beating, the packet is opened, and each leaf of gold is taken out, and cut with a knife into four equal squares, thus increasing the 150 pieces to 600 of nearly the same size as at first. These are put between the leaves of another tool, called a *shoder*, made of *gold-beater's skin*. This substance is the cæcum of the ox, which is first doubled, then prepared with solutions of alum, isinglass, white of egg, &c., and after being beaten between folds of paper to expel the grease, is finally pressed and dried. The shoder is inclosed in parchment and beaten as before, but with a smaller hammer, about 9 or 10 lbs. weight, till the squares of gold are again extended to nearly the size of the skins. The shoder requires about two hours' beating for this purpose. During this period the packet must be often folded, to render the gold as loose as possible between the membranes. As all the leaves do not spread quite equally, the shoder is beaten upon after the more expanded leaves have reached the edges, the effect of which is, that these come out of the edges in the shape of dust, and this allows time for the smaller leaves to reach the full size of the shoder.

The packet is now opened, and the leaves of gold, being spread on a cushion, are again subdivided into fours, by means of two pieces of cane cut to very sharp edges, and fixed down crosswise on a board. This rectangular cross being applied on each leaf, with slight pressure, divides it into four equal portions, and is preferable to a steel knife, to which the gold, in its now attenuated state, would be liable to adhere. The 2400 squares thus formed are separated into three parcels of 800 each, and the squares of each parcel are placed in another shoder or mould composed of gold-beater's skin, inclosed in the parchment cases, and beaten as before. This is the last and most difficult stage of the process. The mould must be made of the finest skins, about 5 inches square; and on the fineness of the skin, and the judgment and dexterity of the workman, the perfection and thinness of the leaf of gold depend. A 7 lb. hammer is now employed, and after two hours' beating the gold is reduced to the $\frac{1}{150000}$th of an inch in thickness, and begins to transmit the rays of light. When the gold is quite pure, or but slightly alloyed, it transmits the green rays, but in gold highly alloyed with silver, the pale violet rays are transmitted. After being hammered another two hours, the leaves acquire the tenuity of ordinary leaf-gold, and average from 3 to $3\frac{1}{2}$ inches square. The three beatings and two quarterings expand the gold to an area about 190 times greater than it had in the form of a riband, and 100 square feet of it weigh only an ounce. It is true that an ounce might be hammered to cover an area of 160 feet; but in this case the gold would be too much attenuated for common use, and the extra labour and care required would not be compensated by any corresponding advantage. After the last beating, the leaves are lifted one by one with a delicate pair of long pincers, made of white wood, and are spread out on a leathern cushion by blowing them flat with the mouth. Broken or blemished leaves are rejected; the good ones have the ragged edges cut off with a square frame of sharp cane, which reduces them all to a uniform size, and are then placed in a book, the leaves of which have been rubbed with red ochre, to prevent the gold from adhering. Each book is capable of holding 25 leaves, and in this form the gold-leaf is sold for gilding picture-frames and books, and for the various ornamental purposes to which it is applied in the arts.

In this country the art of gold-beating was long confined to London, where it has been carried to higher perfection than in any other part of the world; but of late years efforts have been made on the Continent, with the aid of English gold-beaters' skin, to emulate the beauty and fineness of the English product; and the art is now practised successfully in different large cities in England, as well as in Scotland and Ireland. At the Great Exhibition of 1851 machines were exhibited for superseding the arduous operation of beating gold by hand; but the success of these was very partial, and no material change has taken place in the process as above described since that date, the gold-leaf at the present day being made almost entirely by hand.

Gilding.—This consists in applying a superficial covering of gold to articles of wood, metal, &c., chiefly for the purpose of ornament, but sometimes also for utility, as when it is essential that the article should be preserved from tarnishing. Gilding is practised by various methods, the principal of which may be classified under the following heads, namely:—1. Mechanical gilding with gold-leaf for wood, leather, &c.; 2. Chemical gilding, properly so called, which is practised on metallic substances, and includes wash-gilding, or gilding by amalgamation; gilding by immersion and various other processes; 3. Electro-gilding, or the deposition of gold by the electrolysis of its solution.

1. *Mechanical Gilding*, or gilding on wood with gold-leaf, is of two kinds, distinguished as burnish-gilding and oil-gilding.

The process of *burnish-gilding* may be exemplified as applied to a picture-frame. In this case the gilder receives from the joiner a bevelled moulding 12 feet in length, which he prepares for gilding by a number of preliminary coatings of size, mixed with different substances. He first gives it a priming of hot size and whiting, this mixture being laid on in a somewhat fluid state, and therefore termed *thin-white*. It is prepared by melting the size in an earthen pipkin, and stirring in the whiting in fine powder by small portions at a time. When this first coating is dry the surface is examined, and all holes and irregularities are filled up with a mixture of whiting and size, made of the consistence of putty, but containing no oil. The moulding then receives 4 or 5 layers of a mixture similar to the first, but of greater consistence, and therefore termed *thick-white*, allowing time between each layer for the work to dry. While each of these last coatings is still wet, the fine work of the moulding is kept open by means of chisels, gouges, and other tools for the purpose. Sometimes two thick-whites are laid on successively, without allowing the first to dry, and are then worked into the shape of the moulding by hard stones of the required form. The whiting is now from one-sixteenth to one-twelfth of an inch in thickness, and is trimmed to remove unevenness at the edges, after which the entire surface of the moulding is smoothed with pumice-stone, formed to fit exactly into the various parts, which are slightly wetted to promote the smoothing effect. A final polish is given to the whiting by glass-paper.

The moulding is now ready to receive the gold-size, which consists of pipe-clay, red chalk, black lead, suet, and bullock's blood. Of this mixture, which is sold to the gilder in a tenacious mass, rather softer than butter, a portion is melted with common clear thin size; and while still slightly warm is laid on with a brush, and with great nicety of hand.

The next operation is the gilding, for which several tools are required—a leathern cushion to receive the gold-leaf, a knife for cutting it into

different sizes, and a little instrument, termed a *tip*, for laying the leaf on the moulding. This last instrument consists of two pieces of card glued together, with the ends of a row of camel's hairs fastened between them, and projecting from 1 to 1½ inch. The gilder having moistened with water a few inches of the moulding about to be gilded, and having cut a leaf into stripes suited to the width of the part on which it is to be laid, touches one of these stripes with the tip, to the hairs of which it slightly adheres, and transfers it to the moistened part of the moulding When the whole of the moulding has been thus covered, it is set aside to dry.

The burnishing is performed by rubbing briskly over the gold a piece of flint or agate. This greatly increases its brilliancy, and does not injure the gold-leaf on account of the foundation of gold-size and whiting which yields under the hand. The parts which are to be in *dead* gold or *matt* are left unburnished, but over these a very thin clear size is passed, and when dry the gold is carefully wiped with soft cotton wool. The work is completed by wetting the matt parts with a pencil dipped in clear finishing size. The moulding is then passed into the hands of the frame-maker, who cuts it up and forms it into a frame of the required size.

When the frame or other article to be gilt is somewhat richly ornamented, *oil-gilding* is resorted to. In this case the moulding is first whitened as before, but is then at once made up to the required shape and decorated with composition ornaments before the application of any further primings. In this state the gilder receives the frame, and his first operation is to wash it, in order to free it from oil or other impurities. He then gives it two or three coatings of thin-white, mixed with a little soft clay, and several additional coatings are given to the parts intended to be burnished. Two or three coats of a moderately strong size called *clear-cole* are now spread over the whole, after which the *oil gold-size*, consisting of a mixture of boiled linseed-oil and ochre, is laid on smoothly with a brush. After six or eight hours, when the oil-size has been partially dried, the gold-leaf is applied as before, except that in this case no water is used, the oil serving the same purpose. For deep ornaments the gold is pressed in with cotton-wool, and in this case the gilding has to be repeated to remove the irregular fractures known by the gilders as *spiders' legs*. The work, which has still a ragged appearance, is now carefully gone over and smoothed with a brush—superfluous gold being removed from some parts and worked into others. This operation is termed *skewing*. The parts to be burnished are then treated as before, and finally the frame, after being dusted, is sized with clear size and yellowed on the outside.

Another application of gold-leaf is to book-gilding. When the book is bound in leather, the back and sides to be gilt are first covered with a coating of isinglass, or white of egg, dissolved in a large proportion of water, and termed *glaire*. This is allowed to dry, and when the gold-leaf is about to be laid on, a woollen rag, slightly moistened with hog's lard or sweet oil, but so as to feel almost dry to the touch, is rubbed over the leather. This causes the adherence of the gold-leaf, which is laid on over the whole space intended to be covered by the figure; and is then imprinted with a hot brass block, cut to the required design or letters. For this purpose a blocking-press is employed, and in the upper bed is a cavity containing a row of gas jets for keeping the block at the proper temperature; the superfluous gold is readily brushed off the parts which have not received the impression. Books bound in cloth are treated in the same manner, except that they do not receive the preliminary coating of glaire, as this is replaced by a portion of the glue under the cloth being raised by the heated block. The edges of the leaves of books are gilded in the bookbinder's press by applying a solution of isinglass or white of egg, moistened with oil, and then laying on the gold-leaf, which is firmly pressed down and burnished with agate, bloodstone, or polished steel. Instead of isinglass or albumen, the serum of bullock's blood is often employed.

Chemical Gilding.—Metallic surfaces may be gilded either by applying the gold in the state of an amalgam, an operation which is termed *water* or *wash-gilding*, or by introducing the articles into a suitable solution containing gold, when this metal is deposited, owing to the chemical action which takes place. This latter is called gilding by *immersion*.

Water or *Wash gilding* consists in applying evenly an amalgam of gold to the metallic surface to be gilt, and then dissipating the mercury by heat so as to leave on the surface a film of pure gold. Ordinary brass answers very well for gilding on, but the alloy which is now generally preferred is a mixture of copper, nickel, and zinc, which may be so proportioned as nearly to resemble gold in colour. To form the amalgam, a small quantity of gold, reduced to grains or thin plates, is heated in a crucible till it becomes faintly red, and then thrown into mercury, also previously heated till it begins to emit visible vapour. The proportion of mercury to gold is generally as six or eight to one. The mercury is then stirred with an iron rod till all the gold is dissolved. The crucible containing the two metals is now removed from the fire, and the amalgam thrown into water, where it separates itself from the excess of mercury as a pasty mass; the whole is then squeezed in a bag of chamois leather in order to remove this superfluous mercury, which however contains gold, and is therefore employed in subsequent operations. The amalgam left behind is of the consistency of butter, and contains about 67 per cent. of gold and 33 of mercury.

Before the application of amalgam to the surfaces of articles to be gilded, they must undergo several operations in order to remove grease, &c., which would prevent contact between the metal and the amalgam: these are *annealing*, *pickling*, and *cleansing*.

The first of these is performed in a brick oven in which is placed an iron grate containing in-

candescent charcoal, by which the objects are raised to a cherry red heat, when they are removed and allowed to cool in the air. A superficial layer of oxide having been thus produced, it is removed by the second treatment or pickling, which consists in first dipping them in very dilute sulphuric acid and then scrubbing them with a hard brush. On their removal from the acid bath they present a speckled appearance, in order to remove which they must be subjected to the last of these preliminary operations, *cleansing*. They are rapidly dipped in a bath of ordinary nitric acid, which contains small quantities of sulphuric acid and common salt, and finally dried in hot sawdust. The metallic surface is now rubbed over with a solution formed by dissolving 100 parts of mercury in 110 parts, by weight, of nitric acid, of specific gravity 1·33, and diluted with about twenty-five times its weight of distilled water. This solution not only helps to cleanse the metal from any tarnish, but in consequence of the stronger affinity of the copper alloy for nitric acid than the mercury has, the latter is precipitated upon its surface in the same manner as a piece of polished iron precipitates copper from a solution of the sulphate of that metal. The amalgam is now spread evenly over the alloy to be gilt by means of a brush, and readily adheres to the metallic surface in consequence of the thin film of mercury already deposited upon it. Generally, however, the nitrate solution and amalgam are applied simultaneously. For this purpose a gilder's scratch-brush, made with fine brass-wire, is first dipped into the nitrate of mercury solution, and is then drawn over a lump of amalgam, placed on the sloping side of an earthen vessel, after which the brush is applied to the surface of the alloy. This process is repeated till the whole is coated with its just proportion of gold. The article is then bathed in water, dried, and exposed to a fire of glowing charcoal to expel the mercury. The heat applied must be just sufficient for this purpose, and the article must be turned about to expose it equally on all sides. From time to time it is withdrawn from the fire, and while the operator holds it in his left hand, protected by a stuffed glove, he spreads the amalgam equally with his right hand by means of a long-haired brush. The piece is then returned to the fire, and the same operations are repeated till the mercury has entirely volatilized. This is known by the surface becoming of a dull yellow colour, and by the hissing sound when a drop of water is let fall upon it.

The surface, now coated with a film of gold, is still deficient in polish and lustre. To communicate these qualities it is washed and well rubbed with a scratch-brush in water acidulated with vinegar. It is then covered with a composition called *gilding wax*, which is simply a mixture of bees' wax with some of the following substances, namely, red ochre, verdigris, copper scales, alum, vitriol, and borax. Coated with this composition, it is again exposed to the fire until the wax is burnt off. By this means the gilding is found to be intensified in colour, probably in consequence of the complete dissipation of some of the mercury remaining after the former operations. If the article is wrought or chased, the parts to be burnished are now rubbed with a steel burnisher and dipped in acidulated water till a fine metallic lustre is produced. Formerly hæmatite or bloodstone was used for this purpose, but they are now generally replaced by the steel burnisher, which is case-hardened and then carefully polished. The parts to be dead are coated with a mixture of sea-salt, nitre, and alum, fused in the water of crystallization of the last-mentioned salt; the article is then heated till the saline crust with which it is covered enters into fusion and becomes homogeneous, after which it is withdrawn and suddenly plunged into cold water, which entirely detaches the crust. Lastly, the piece is passed through weak nitric acid, washed in pure water, and dried.

The actual weight of gold deposited on the metallic surface varies from about ·067 to ·258 grain per square inch.

Gilding by Immersion is another method by which copper trinkets and stamped articles can be coated with a thin film of gold. This method, which dispenses with the dangerous use of mercury, so detrimental to the health of the workmen, was patented by Mr. Elkington, of Birmingham, in 1836, and has been very extensively practised, more especially in France. In this process four distinct operations may be enumerated. They are:—(1.) Preparation of the bath. (2.) Preparation of the trinkets, &c. (3.) Gilding. (4.) Colouring.

To prepare the bath 100 grains of fine gold should be dissolved in 250 grains of nitric acid (spec. grav. 1·333) and 250 of hydrochloric acid, 250 grains of water being afterwards added. About $2\frac{1}{4}$ pints of water are now heated in a cast-iron pan, the interior of which is already coated with gold from preceding operations, 3000 grains of bicarbonate of potash being added to it. The same amount of this salt is also added to the chloride of gold solution in very small quantities at a time, after which it is added to the former. The whole is brought to its boiling point, and maintained at it for about two hours, water being added from time to time in order to keep the bulk constant, when the bath is ready for use. The trinkets, &c., are prepared in a manner similar to that already described under *Water Gilding*, the only difference being that after the final operation of "cleansing," there described, they are subjected to that of "brightening," which consists in introducing them into another solution. The best for this purpose consists, according to Bochet, of 40 parts of sulphuric acid (spec. grav. 1·712), 40 parts of nitric acid (spec. grav. 1·342), and 1 part of sea-salt. The mixture should not be used until several hours after being made. When the gold is to have a dead appearance it is advisable to add a small quantity of sulphate of zinc as well. After having passed through the several cleansing operations the washed trinkets are introduced into the gilding bath, in which they

remain for 30 seconds; a longer exposure does not increase the thickness of the film of gold. If on removal the gilding is found to be imperfect, the trinket should be plunged into a weak solution of nitrate of mercury, and again into the gold bath. After being washed and dried in hot sawdust they are subjected to the final operation of "colouring," which consists in immersing them in the solution of 6 parts of nitre, 2 of sulphate of iron, and 1 of sulphate of zinc, after which they are dried over a clear fire, washed, and again dried.

The method above described has several advantages over the old method of water-gilding, the chief of which are:—1. It does away with the pernicious vapours of mercury. 2. There is no difficulty in gilding the most irregular-shaped articles evenly, which would be impossible by the aid of mercury, as the amalgam could not be uniformly applied.

The reaction which takes place in the bath has been studied by several eminent chemists, but the best explanation seems to be that given by Barral. He concludes that for every atom of gold deposited an atom of copper (from the trinket) is dissolved, a fact which proves it to be a protoxide of gold which is decomposed, and not a teroxide. He finds also that chlorate of potash is formed in the bath. The reactions are as shown by the following equation:—

$$6AuCl_3 + 3K_2CO_3 + 6Cu = 6CuCl_2 + 5KCl + KClO_3 + 6Au + 3CO_2.$$

Carbonic acid gas is liberated, and the chloride of copper, in presence of bicarbonate of potash, is converted into an insoluble carbonate.

Gilding on iron and steel cannot be well performed directly by the method of amalgamation, as it is difficult to prevent the oxidation of the metal during the volatilization of the mercury; and the temper of sword blades, daggers, and other such instruments, to which the gilding is usually applied, is liable to be injured in the process. It may be effected, indeed, by previously applying to the polished surface the solution of nitrate of mercury already described, and known as *quicksilver water;* the acid so applied unites with a portion of the iron or steel, and deposits in its place a thin coating of mercury, which combines with the gold amalgam when brushed on. By this method, however, a bright and durable gilding cannot be obtained.

Another not very successful method of gilding on polished iron and steel is by means of an ethereal solution of terchloride of gold. For this purpose the gold is first dissolved in aqua regia, and about twice the quantity of ether is then cautiously added in a large vessel. The liquids are agitated and allowed to rest, when the ether separates and floats on the surface of the acid. The whole mixture is now poured into a funnel terminating in a small closed aperture, and again allowed to settle and separate, after which the acid is run off from below. The ether which remains has taken up all the gold, and before applying it to the iron or steel the metal is polished with the finest emery and spirits of wine. The ether is then laid on with a small brush, and as it evaporates it deposits the gold, which can now be heated and polished. This gilding, however, is neither very rich nor durable, in consequence of the affinity between gold and iron being feeble compared to that between gold and copper or silver.

But polished iron and steel, as well as copper, may be effectively gilded with gold-leaf by the application of heat. For this purpose the metals are heated to such a temperature as to give iron a bluish tint. The first coat of leaf-gold is then applied, being pressed gently down with a burnisher, and then exposed to a moderate heat. Several leaves, either single or double, are thus successively applied, and the last is burnished down cold. This is the method usually practised in gilding iron or steel.

Gilding on silver may be performed by means of the ashes of a linen rag, which has been dipped in a solution of gold and copper in aqua regia. For this purpose 60 grains of fine gold and 12 of rose copper are dissolved in 2 ozs. of aqua regia. With this solution a quantity of linen rags sufficient to absorb all the liquid is soaked. The rags are then dried and burned, and the ashes contain the gold in powder. A moistened cork or piece of leather is dipped into this powder, and after the article to be gilt has been well annealed and polished, the ashes are rubbed over it with the cork till the surface appears sufficiently gilded. Large articles are finally burnished with bloodstone, and small ones with steel burnishers, soap-water being, at the same time, applied.

Gilding on glass or porcelain is effected with pulverulent gold, or gold precipitated from its chloride solution by means of sulphate of iron. In this state it is mixed with one-twelfth of its weight of oxide of bismuth, together with a small quantity of borax and gum-water, and is applied to the parts to be gilt with a camel's hair pencil. The article is then heated in a muffle, and when removed the gold appears of a dingy colour, but the lustre is brought out by burnishing with agate or bloodstone. Lastly, it is cleaned with vinegar or white-lead.

Vessels which are not often used, and are not liable to wear, may easily be gilt in a less durable manner, by fixing gold-leaf upon them with copal varnish.

3. *Electro-Gilding.*—This process, which has now almost entirely superseded the method by amalgamation, is applicable not only to metals, but to wood, plaster, or any other substance capable of receiving a coating of plumbago, or of Parkes' patent preparation of phosphorus. Full details of this beautiful process have been given in the article Electro-metallurgy, to which the reader is referred.

Artificial Gold.—Under the name of Californian, Abyssinian, and Oroide gold, and other sounding titles, are sometimes sold alloys which do not contain one grain of the precious metal, but merely resemble it in colour and lustre so long as they remain untarnished. It is stated that a good imitation may be formed of the following:—Pure copper, 100 parts by weight; zinc, 17; magnesia, 6; sal ammoniac, 3·60; quicklime, 1·80; tartar, 9. The copper is melted in

a crucible, in a suitable furnace; the magnesia, sal ammoniac, lime, and tartar are then added, separately and by degrees, in the form of powder; the whole is stirred for about thirty minutes to thoroughly mix the ingredients, and the zinc is then thrown on the surface, having first been ground into very small grains; the stirring is continued until the fusion is complete. The crucible is now covered, and the fusion continued for about thirty-five minutes, when it is uncovered and skimmed with care, and the contents are run into a mould of moist sand or metal. The material which results may be cast at such a temperature that any ornamental form may be given to it. It is very fine-grained, and is also damascene, malleable, and capable of taking a very brilliant polish. When tarnished by oxidation, its brilliancy can be restored by a little acidulated water. If tin be employed instead of zinc, the alloy will be still more brilliant.

Compounds of Gold.—Gold is known to form compounds with oxygen, sulphur, and the haloids—chlorine, bromine, iodine, cyanogen, &c., but the number of its compounds is few in comparison with most other metals.

Oxides.—These are two in number, namely:—(1.) The suboxide or protoxide (Au_2O), which may be precipitated as a dark green powder by adding a dilute solution of potash to a solution of the protochloride of gold. If this precipitate be treated with ammonia, fulminating gold is formed; an extremely dangerous substance, exploding with fearful violence, in consequence of which its composition has not, as yet, been accurately determined. Heated to about 250° C. (482° Fahr.), this oxide is decomposed into oxygen and metallic gold.

(2.) Peroxide, or anhydrous auric acid (Au_2O_3), may be prepared in several different ways. The method usually given is analogous to the above for preparing the protoxide, and consists in decomposing a solution of the terchloride of gold by means of magnesia or oxide of zinc: insoluble aurates of magnesia or zinc are formed, which on being treated with cold dilute nitric acid yield hydrated auric acid, from which anhydrous auric acid may be obtained by heating at 100° C. (212° Fahr.), in order to expel the water. M. E. Fremy gives a somewhat complicated method for preparing this oxide in a state of purity, which is too long to be given here in detail, and for which the reader must therefore be referred to the "Traité de Chemie" of MM. Pelouze and Fremy, tome iii. p. 1209. It consists in the preparation of aurate of potash by means of terchloride of gold and potash, and from this aurate the auric acid is subsequently extracted by sulphuric acid. It is a brown or yellow powder (the colour varying with the strength of acid used), and is readily reduced by light or a temperature of 245° C. (473° Fahr.) to metallic gold and oxygen. Carbon, boiling alcohol, and nearly all the organic acids (especially oxalic) have the same power of reduction. It is soluble in the haloid acids, forming the salts referred to below. As is the case with the protosalt, when treated with ammonia, fulminating gold is produced in a manner analogous to that in the case of silver. Auric acid forms salts termed aurates. Thus we have the aurate of potassium ($KAuO_2,3H_2O$), a solution of which may be used in electro-gilding.

Sulphide.—When sulphuretted hydrogen gas is passed through a cold solution of terchloride of gold, a bisulphide (Au_4S_4) is produced, which however is unimportant. If instead of a cold solution it be boiling, the aurous sulphide (Au_2S) is formed. It is a dark brown or black powder, which combines with the protosulphide of potassium or sodium, forming double salts. The former of these is employed in the arts for the purpose of gilding china, and goes by the name of *Burgos lustre.*

Chlorides.—Gold and chlorine form two distinct compounds, namely, the protochloride (AuCl) and the terchloride ($AuCl_3$).

The *protochloride* is formed by gently heating the terchloride to a temperature of about 200° C. (392° Fahr.), when a portion of the chlorine is expelled, leaving a pale yellow salt, which is decomposed on exposure to light.

Terchloride.—This, the most important compound of gold, is obtained when gold is dissolved in aqua regia, and if this solution be evaporated to dryness at a temperature not exceeding 250° Fahr. (taking care to have an excess of hydrochloric acid), the salt will be obtained as a red deliquescent difficultly crystallizable mass. It is decomposed by either light or heat into free chlorine and protochloride of gold, and if the heat be too great this is further decomposed into chlorine and metallic gold. It is a remarkable fact that although this salt is decomposed at 200° C. into Cl and AuCl, and at a still higher temperature into Au and Cl; yet $AuCl_3$ may be sublimed and then obtained in crystals of a considerable size, even at temperatures higher than that at which it is usually decomposed. The perchloride is very soluble in water and alcohol, also in ether, and this latter solution was formerly used in medicine under the name of *potable gold;* it was also used for the gilding of steel. In combination with hydrochloric acid it forms a yellow crystalline salt, which is very soluble in water; and from this solution, by evaporation, the long yellow crystals may be obtained. If treated with caustic potash, aurate of potassium and chloride of potassium are produced; and as with the oxides, the addition of ammonia causes the formation of a yellow precipitate of fulminating gold. An immense number of substances have the power of depositing gold from its solution in aqua regia, among which may be mentioned carbonic oxide, phosphorus, nitric dioxide, many animal and vegetable substances, most metals, sulphurous and phosphorous acids, salts of protoxide of mercury and of protoxide of iron, &c. Some of these afford a convenient method for the preparation of pure gold, as has been described on p. 68. The gold is in many cases deposited in minute particles, which give a red or purple colour to the solution, and Faraday made some interesting discoveries with

reference to the changes in these colours. Thus, when the bottle containing the solution was chemically clean, the particles remained suspended for months, giving a ruby red colour to the liquid by transmitted light, but it appeared to be turbid and brown by reflected light. On adding a little common salt this coloration entirely disappears, and the gold is in the course of a few hours deposited as a purple powder. The perchloride forms several double chlorides, the chief being those with potassium, sodium, and ammonia. Gold combines with iodine, forming two iodides (AuI and AuI_3), which correspond in composition with the chlorides; these however are unimportant, as is also the only compound of gold and bromine, namely, the terbromide ($AuBr_3$).

The *cyanides*, two in number, also correspond in composition with the chlorides. They have a great tendency to combine with other cyanides, especially those of the alkalies and alkaline earths.

The protocyanide (AuCy) may be prepared in the following manner. Fulminating gold is prepared as before described by the addition of ammonia to perchloride of gold. It is then dissolved in cyanide of potassium with the application of heat. On cooling, crystals of the double cyanide of gold and potassium are deposited. If these be now dissolved in hydrochloric acid, evaporated to dryness, and mixed with water, a yellow insoluble powder remains behind, which is the protocyanide of gold, and should be washed and dried in the dark. It exists both amorphous and crystalline, and is easily decomposed by heat. The most important of the double cyanides is that of gold and potassium ($AuKCy_2$), largely used in electro-gilding, for which purpose it may be prepared by dissolving in warm water 77 parts of the protocyanide of gold, and 23 parts of cyanide of potassium, and evaporating the liquid; the double cyanide remaining behind in the form of colourless prismatic crystals.

The percyanide ($AuCy_3$) is an unimportant salt prepared by treating the percyanide of gold and silver ($AgCy,AuCy_3$) with hydrochloric acid; evaporating the solution in a vacuum, and redissolving in water, out of which the salt is crystallized by concentration.

Fulminating Gold.—As mentioned in the accounts of the oxide and chloride of gold, this may be prepared from both of these salts, but although detonating power exists in both cases, the compounds are not identical. In the former (prepared from the peroxide) there is no chlorine present, whereas that prepared from perchloride of gold does contain chlorine. In the one case the colour is dark greyish, whereas the presence of chlorine imparts a yellow colour to the fulminate. It is possible to decompose it without detonation by heating with from 20 to 30 times its weight of sulphate of potassium. To the first form Berzelius gives the formula $Au(NH_4)O_2NH_3$, or $AuIIO_2,2NH_3$; whereas Dumas considers it to be more correctly expressed by $Au_2N,NH_3,3H_2O$. This latter chemist gives the following as the result of an analysis of the form containing chlorine:—

Gold	73·0
Chlorine	4·5
Nitrogen	9·8
Hydrogen	2·2
Oxygen	10·5
	100·0

The composition therefore of fulminating gold, as deduced from these percentages, is expressed by the formula—

$$Au_3ClN_6H_8,5H_2O.$$

Both preparations are extremely dangerous, detonating by a slight blow, by friction, by a slight heat, or often even spontaneously. They should therefore only be prepared in very small quantities at a time.

Purple of Cassius.—When a mixture of protochloride and bichloride of tin, very much diluted, is added drop by drop to a dilute neutral solution of terchloride of gold, a flocculent purple deposit is formed, which has been termed *purple of Cassius*, from the circumstance that the method of preparing it was first described by Andreas Cassius of Leyden and his son, in 1685, and they called it *gold purple*. It may likewise be prepared by fusing together 150 parts of silver, 20 of gold, and 35·1 of tin, and acting on the alloy with nitric acid, which dissolves out the silver, and leaves a purple residue containing the tin and gold. To prevent the oxidation of the tin during the fusion the three metals should be projected into a red-hot black-lead crucible, which contains a little melted borax. Fuchs states that the finest purple is produced by mixing a solution of sesquichloride of iron with aqueous protochloride of tin, till the yellow colour is converted into pale green, and precipitating the gold solution with the mixture thus formed; he adds that the protochloride of iron in the liquid does not affect the product.

If while this powder is moist on the filter it be washed with ammonia, it is dissolved, and a splendid purple liquid passes through. From this liquid the colouring matter separates only after standing for several weeks. To obtain a gold purple of constant composition the following method is recommended by Pelletier:—20 grammes of gold are dissolved in 100 of aqua regia, made by the addition of 20 parts of nitric acid to 80 of commercial hydrochloric acid, the solution being evaporated to dryness in a water bath. The residue, after being dissolved in water, is filtered and diluted with 7 or 8 decilitres of water, and placed in contact with tin filings, a vigorous action ensues, and in a few minutes the liquid becomes brown, and deposits a purple precipitate, which should be washed and dried at a gentle heat.

This purple possesses the following composition:—

Stannic acid	32·746
Protoxide of tin	14·618
Protoxide of gold	44·772
Water	7·864
	100·000

Other modes of preparation have also been recommended, which however need not be described.

This substance, in the moist state, is dark purple-red, and after drying brown. Its true nature and composition have given rise to much discussion. According to some authorities it contains metallic gold with hydrated stannic oxide; according to others the gold is oxidized. Berzelius concluded from the researches of M. Figuier, that it consists of a hydrated double stannate of gold and tin, as expressed by the formula—

$$SnAu_2Sn_2O_34H_2O.$$

It seems certain that whatever the composition be before ignition, after this has taken place the powder consists of a mixture of stannic oxide (SnO_2) and metallic gold; but the fact of the powder in its unignited state being soluble in ammonia, and not yielding any gold when treated with mercury, appears to be convincing proof that free gold does not then exist.

The composition assigned by Berzelius, which has been confirmed by M. Barral, accounts for the principal reactions of the purple of Cassius. Thus, heat decomposes it, and expelling water leaves behind a mixture of gold and stannic oxide.

Purple of Cassius is decomposed by the acids, but is not changed by the action of light. Hence it is somewhat extensively employed in the arts, chiefly for colouring glass and porcelain. When mixed with a little borax or some fusible glass, and applied to the surface of china, it imparts to it a beautiful rose or a rich purple colour. Its different applications as a colouring material have already been explained in the articles Enamels and Glass. It is remarkable that the oxide of tin does not appear to be essential, since even finely-divided metallic gold alone will give the same purple hue.

Spectrum of Gold.—Huggins has observed no less than twenty-three lines in the spectral band produced by gold, but of these only six are of importance, the others being so faint as to be barely visible. The two brightest (equal in intensity to the well-known D lines of sodium) occur one in the yellow-green near to E, and the other in the green between E and *b* of Fraunhofer's lines. Of the four other important lines, three occur in the yellow-orange between C and D, and one, possessing a high refrangibility, in the blue between F and G.

Recently Lockyer has suggested the use of the spectrum of gold in connection with that of copper as a means of determining the amount of gold contained in a given alloy, thus superseding the ordinary method of assay. A number of experiments have been made by him, and in the Royal Mint, on the subject, and a paper was read before the Royal Society by Lockyer and Roberts; but as yet no practical application has been made of the discovery.

Quantitative Estimation of Gold Ores and Alloys.—In proceeding to determine the exact amount of gold present in an ore or alloy, it is obviously necessary to exercise the greatest caution in the sampling. Excellent advice on this point is given by Percy in his admirable lecture on the metallurgical treatment and assaying of gold ores, delivered at the Museum of Practical Geology. Careless sampling, he remarks, can only mislead; assays of individual specimens may be accurate, but they are worse than useless if the assayer has not operated upon an *average* sample of the ore. He therefore advises the capitalists, to whom prospectuses of gold-mining schemes may be submitted, not to be allured with glittering specimens of gold ore, with assays yielding a high produce, and with the glowing statements of sanguine promoters or enthusiastic adventurers, without having ascertained on good evidence that the samples which are presented to his notice are really *average samples* of the ore, and that something like a continuous supply may reasonably be expected. If such specimens, he adds, do not represent an average, they become what the Cornish miner calls *slocking-stones*, which are at all times enticing and dangerous to the inexperienced and unwary, and never more so than in the case of auriferous ores. The sampling generally devolves upon the miner, but the assayer and metallurgist should likewise understand the business. Assayers of great experience and high integrity may occasionally, he adds, commit unintentional mistakes. Thus, a few years ago, two small pigs of lead from South America, very rich in silver, were offered for sale. Portions had been taken from the top and bottom of each pig, with a view to obtain a fair average. Percy had occasion to attempt to verify the report of the assayers. Portions were taken from the same parts of each pig as in the first instance; but the results did not agree with the report, nor did Percy's assays agree with each other on taking fresh portions. It was therefore certain that the composition was not uniform, and that the portions taken for the purpose of assaying in neither case represented an average. The pigs were accordingly sent again to the same assayers. Each pig was melted separately, and while melted a sample was taken. A second report was given, which differed from the former to the extent of 1000 ozs. to the ton! In the sampling of gold ores most especial care should be taken, as the precious metal exists irregularly diffused through the mass, in particles of very different size, and as minute errors in sampling will necessarily be greatly multiplied when the quantity of gold per ton is calculated from the assay of, it may be, 500 or 1000 *grains* of ore.

The quantitative estimation may be made, more or less correctly, by one of four methods:—1. By determining the specific gravity of the ore or alloy; 2. By the touchstone; 3. By chemical analysis, or the *wet method* of assaying; and 4. By the metallurgical, or *dry method*, in which fire is the principal agent. The first two afford only approximations, and the second is applicable only to alloys of gold; but both may be useful when circumstances render impossible or inconvenient the performance of an exact assay by the wet or dry method.

1. *Quantitative Estimation by Specific Gravity.*—It is evident that the high specific gravity of gold not only affords facilities for separating it, by means of washing, from other matters, but also for estimating

approximatively the amount in which it is present in any ore or mineral of known composition. The nature of the other ingredients being ascertained, and consequently their weight or specific gravity, the additional weight must be due to the presence of gold, and hence its amount may be calculated.

But it is obvious that in the case of alloys this method is only applicable provided the specific gravity of the alloy is accurately identical with that which would be calculated from the relative amounts and specific gravities of its constituents. This, however, is rarely the case, and the results obtained by this method can only be considered as very rough approximations, except in the case of nearly pure gold, such as that found in Australia. The actual specific gravity of native gold alloys is invariably *lower* than that calculated; hence the results obtained by this method will give a *lower* assay than the amount of gold really warrants.

Taking for granted that the mineral proposed to be submitted to this test is a piece of auriferous quartz —the first point to be determined is its specific gravity, or its weight as compared with that of an equal bulk of distilled water; because, if this be no higher than that of common quartz, which is found by experiment to average 2·6, it will be unnecessary to proceed further; but if higher, the amount of gold present may be calculated from the difference.

It is unnecessary here to describe the ordinary methods of determining the specific gravity of a body; any one of those applicable to a body insoluble in water may be used.

Let G represent the weight of gold contained in the quartz or rock.

R	"	weight of quartz or rock.
g	"	specific gravity of gold.
r	"	" of quartz or rock.
W	"	weight in air.
W′	"	" water.

Then the weight of the gold is determined directly by the following formula—

$$G = \frac{g\,W - r\,g\,(W - W')}{g - r}$$

and the weight of pure quartz or rock, if required, by this formula :—

$$R = \frac{r\,g\,(W - W') - W\,r}{g - r}$$

2. *Quantitative Estimation by the Touchstone.*—Another method of estimating approximately the amount of gold, not in auriferous ores, but in native gold or artificial alloys, is by the use of the touchstone, a method which may be practised with considerable advantage, when the apparatus and reagents necessary for the carrying out of a complete assay cannot be conveniently procured. It is especially applicable to the estimation of trinkets or other finished articles, which could not be submitted to the assaying processes, either by the wet or dry method, without destroying them.

The touchstone test consists essentially in rubbing some convenient part of the object to be examined on a smooth piece of black basalt or pottery, which for this reason is termed the *touchstone*, and comparing the marks so formed with those produced by one or other of a series of small bars or needles, consisting of alloys of gold with silver or copper, or both, in known proportions.

The material commonly employed as the "touchstone." and commonly known by either that name or as Lydian Corneine (in consequence of its having been formerly found in Lydia), is a species of basalt of a dark colour found in considerable quantities in Saxony, Bohemia, and Silesia.

According to Crookes five series of prepared touch needles are required. The first consists of copper and gold, and is called the *red series*, the proportion of gold increasing by half carats (equal to 20·9 thousandths), in the successive needles. The second series consists of gold and silver, and is called the *white series*, and the gold increases as in the first set. In the third or *mixed series*, silver and copper in equal proportions are used for the alloying metal, while in the fourth and fifth series the silver and copper are to each other in the proportions of 2 : 1 and 1 : 2 respectively. In all these series the amount of gold varies in the same manner as in the first. The *test acid* usually employed consists of a mixture of 98 parts of nitric acid of spec. grav. 1·340, 2 parts hydrochloric acid of spec. grav. 1·173, and 25 parts of distilled water. Levol recommends a mixture of 123 parts nitric acid, having a spec grav. of 1·274, and 2 parts hydrochloric of 1·173.

In proceeding to make an assay by this method, the first streak obtained by rubbing the object to be examined on the touchstone cannot be safely employed to ascertain its composition if it be a manufactured article, because, by a process previously described, the surface of jewellery is invariably rendered of a higher standard than that of the mass. The object must therefore be passed once or twice over the back or edge of the stone, in order to remove the superficial film of richer metal, before making the streak from which its quality is to be judged. Other streaks are then made successively with two or three of the needles which the assayer, guided by experience, considers to approach nearest in composition to the article under examination. In doing so he compares, not only the colour of the streaks made upon the touchstone, but likewise the sensation of roughness, dryness, smoothness, or greasiness which the texture of the rubbed metals excites when abraded by the stone. When he succeeds in obtaining with one of his needles a streak which is perfectly similar in appearance to that produced by the article under examination, he then moistens both streaks with nitric acid, and this affects them differently if they be not similar in composition.

The test acid above described is also employed. The streak which contains the least gold will be most affected, and on the contrary, the purer the gold the less will it be affected by the acid. Indeed pure nitric acid produces barely any affect when the alloy contains 15 carats gold and upwards, while the test acid is so composed as to cease to work when the alloy contains 18 carats or over. Should the actions

in the two cases fail to correspond, the assayer's experience will enable him to judge in what they differ, and will direct him in selecting another needle to submit to the same comparative test. When one has been found which agrees satisfactorily in all particulars with the metal submitted to examination, the latter is assumed to be of a standard of fineness similar to that which is indicated by the mark on this particular needle.

Although the results obtained cannot be relied on where absolute accuracy is required, yet they afford a useful approximation, not only in estimating the value of manufactured articles which cannot be submitted to a regular assaying process, but also in obtaining that preliminary knowledge of the general composition of an alloy, which is so important to the assayer in proceeding to a detailed analysis. The touchstone is therefore of great use in practised hands, but it is of little avail in the hands of an inexperienced operator.

3. *Quantitative Estimation by the Wet Method—Analysis.*—However useful the approximations obtained from the specific gravity of an auriferous ore, or the application of the touchstone to an alloy of gold, it is evident that more exact methods are required to determine with absolute precision the value of an alloy or ore of this precious metal. Accordingly there are two methods by which the assaying of gold ores or alloys may be conducted with perfect accuracy, and these are distinguished as the *wet* and *dry* methods, according as the agency of liquid solvents or that of fluxes and fire is employed. For practical purposes in the determination of gold the latter process is always adopted, although in the final separation of the silver the dry method, as now practised, involves the application of a liquid solvent.

The principles of the quantitative estimation of gold by the humid method have been already explained in detailing the laboratory process for the preparation of pure gold, and in describing the application of the tests or reagents by which its presence is detected. It is evident that any of the qualitative tests, the application of which results in the precipitation of the gold from its solution in aqua regia, such as protosulphate of iron, may be converted into the means of obtaining a quantitative estimation, by simply weighing the amount of ore or alloy on which the experiment is performed, and then weighing the amount of pure gold, carefully washed and dried, which is obtained in the form of a precipitate. It will therefore be unnecessary to enter into minute details on the chemical principles involved.

It may be stated, however, that if the substance to be examined be a natural or artificial alloy, composed chiefly of the pure metal, such as the gold dust of California or Australia, the quantity taken for the analysis should not exceed 15 grains. A convenient quantity is 12½ grains, as it is then only necessary to multiply the result by eight to obtain the percentage composition. In performing analyses very small quantities are taken, because it is easier to operate upon a few grains than upon a larger mass; the effect of the reactions is more rapid; there is less waste of materials; and as accurate results can be obtained with a small as with a larger quantity, provided sufficient precaution be taken to operate upon an average sample. If the gold be mixed with earth or quartzose matter, so much of this should be taken as may be judged, from preliminary experiments or other sources of information, to contain the amount of native gold above-mentioned; and this must be triturated in a mortar with great care before subjecting it to the action of the aqua regia—a precaution of less importance in merely testing for gold, but absolutely necessary and essential when it is required to ascertain the exact amount of the precious metal present; for unless the quartz be reduced to a state of the most minute division, it is evident that gold remaining enveloped in the quartz will escape the action of the acid.

For an account of the general methods of the estimation of gold by the wet way, we cannot do better than quote from Fresenius' "Quantitative Chemical Analysis," to which the reader may be referred for more detailed information, especially that relating to the estimation of gold in presence of other metals.

Fresenius recommends that the substance under examination, having been weighed, be warmed with hydrochloric acid, nitric acid being gradually added until solution is effected, or it may be repeatedly digested with strong chlorine water. This latter method is especially applicable when the gold is present in very minute quantities or mixed with other oxides which it is wished to leave undissolved. The gold is always weighed as a metal, and its compounds may be brought into this state—

(*a.*) By ignition.

(*b.*) By precipitation as metallic gold.

(*c.*) By ignition, preceded by precipitation as tersulphide of gold.

(*a.*) This method is applicable to all compounds of gold which do not contain a fixed acid. The compound should be heated in a covered porcelain or platinum crucible, very gently at first, but finally to redness; the residue is pure gold. These results are the most accurate.

(*b.*) In the method of precipitation as metallic gold two cases may occur which may conveniently be considered separately, namely:—

(1.) That in which the solution is free from nitric acid.

(2.) That in which it contains nitric acid.

(1.) If the solution does not already contain free hydrochloric acid, add a little, then add a clear solution of sulphate of protoxide of iron in excess; heat gently for a few hours until the precipitated fine gold has completely subsided; filter, wash with hydrochloric acid first, and afterwards with water; dry and ignite. It will be found preferable to perform the deposition in a porcelain evaporating dish rather than in a beaker.

(2). When nitric acid exists in the solution it should be evaporated on a water bath to the consistence of syrup, adding from time to time hydrochloric acid. Dissolve this residue in water containing

hydrochloric acid, and proceed as directed in (1). It should be noticed that cases may occur in which the residue does not dissolve to a clear fluid, but this is of no consequence.

(*c*). In the case in which ignition is preceded by deposition as a tersulphide, a stream of sulphuretted hydrogen should be transmitted in excess through a dilute solution of the compound under examination. The precipitate thus formed is speedily filtered off without heating, washed, dried, and ignited as directed in (*a*).

In the method (*b*) the liquid should be tested before pouring off, to make sure of the last traces of gold having been deposited. This may be done in the following manner:—When the whole of the precipitate appears to have settled to the bottom, a few drops of the supernatant liquid are taken out on the end of a rod, placed upon a surface of clean white porcelain, and tested with a drop of protochloride of tin. If no purple precipitate be formed, it is a proof that the whole of the gold has been thrown down. If a dark brown colouring, but still no subsidence, be produced, this will indicate the presence of platinum. If any precipitate be observed, more of the sulphate of iron or oxalic acid (which may be used as a substitute just as described in the preparation of pure gold) must be added to effect a complete precipitation of the gold contained in the solution.

The pure gold after ignition is placed in a watch-glass or small capsule, and accurately weighed in a pair of delicate scales, which should be capable of turning with a difference of at least one-hundredth part of a grain. Instead of first counterpoising the dish or capsule, and then adding weights to counterpoise the gold, it is better to begin by placing the capsule *containing the gold* in one pan, and counterpoising both by means of sand, or some other convenient material placed in the other. The gold is then removed from the dish, and weights put in its stead sufficient to restore the equilibrium. The number of grains and fractions of a grain required for this purpose will accurately represent the weight of the gold; and in this method of *weighing by substitution*, as it is termed, any risk of error arising from the possible inequality in length of the two arms of the balance will be entirely avoided.

Supposing the gold to weigh 10·75 grains, and that the amount of alloy submitted to experiment was 12·5 grains, or the eighth part of one hundred, it is evident that $10{\cdot}75 \times 8 = 86$ is the percentage of pure gold present.

4. *Quantitative Estimation by the Dry Method—Assaying.*—The fourth and last method of estimating the amount of gold in an ore or alloy is by the use of fluxes and fire. It is therefore termed the *dry method*, and formerly even the separation of the silver was effected without a liquid solvent, by one or other of the dry processes described in connection with the operation of parting on the large scale; but now the agency of an acid solution is employed in the last part of the process.

This metallurgical method, to which the name of *assaying* strictly applies, is that uniformly followed at the Mint and other establishments where assaying is regularly practised, being not only more expeditious than the wet method, but admitting of a greater number of assays being conducted simultaneously. The wet method is useful for special or occasional assays in the laboratory, where assaying furnaces, cupels, &c., would not be kept constantly in requisition. On the other hand, the dry method is the best where assaying is practised as a business, and where all the apparatus required is therefore in constant efficiency. This method consists in the following processes:—1. The accurate weighing and preparation of the assay piece or sample. 2. Fusion, in the case of ores, to separate earthy and other gross impurities, which may be either performed in a crucible by means of oxide of lead, or by the method of *scorification* with metallic lead. 3. Cupellation, to remove the copper and other base metals by oxidation and absorption. 4. Parting by inquartation, or separation of the silver from the gold, by dissolving the former metal in nitric acid. 5. Final weighing of the resulting "cornet," and applying necessary corrections.

From this enumeration of the different operations which constitute the process of assaying by the dry method, it will be seen that it is little more than a miniature representation of the smelting and refining operations already described. It will therefore be unnecessary to explain the principles on which this important department of the subject is founded, as those already enunciated in reference to the smelting and refining of gold ores apply equally to the assaying of these ores as well as of artificial alloys. The principal feature to be noted is that the assayer operates upon a few grains instead of large quantities, while, at the same time, he must exercise the utmost precaution in attending to the weight and proportions of his materials.

Preparation of the Assay Piece.—It is evident that, as the amount of metal operated upon is extremely small, it is of the utmost importance that the weight of the assay piece should be very accurately determined, both before and after the process. When the alloy under examination is rich, such as that used for the coinage, the assay piece, having been first adjusted by an assistant to as nearly as possible the right weight by means of a balance turning with about $\frac{1}{400}$th of a grain, is re-weighed by the assayer on a superior balance, which should be capable of indicating distinctly $\frac{1}{1000}$th of a grain when loaded with about 12 grains in each pan. Very delicate balances are specially made for this purpose. The most generally approved form now in use is shown in Plate III., Fig. 4. It is made by Oertling of London, and is capable, when new, of indicating $\frac{1}{20000}$th part of an assay pound of half a gramme (7·716 grains), and will always indicate half this amount. It is essential that the balance employed be extremely sensitive, sure, and quick; qualities which require a very light and carefully constructed beam. The beam in the balance shown is 10 inches long, and usually weighs about 125 grains. The

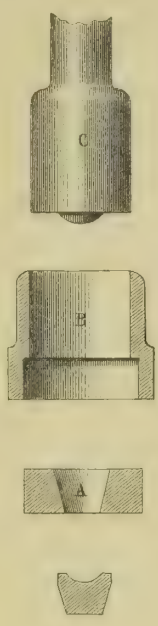


Fig. 1.

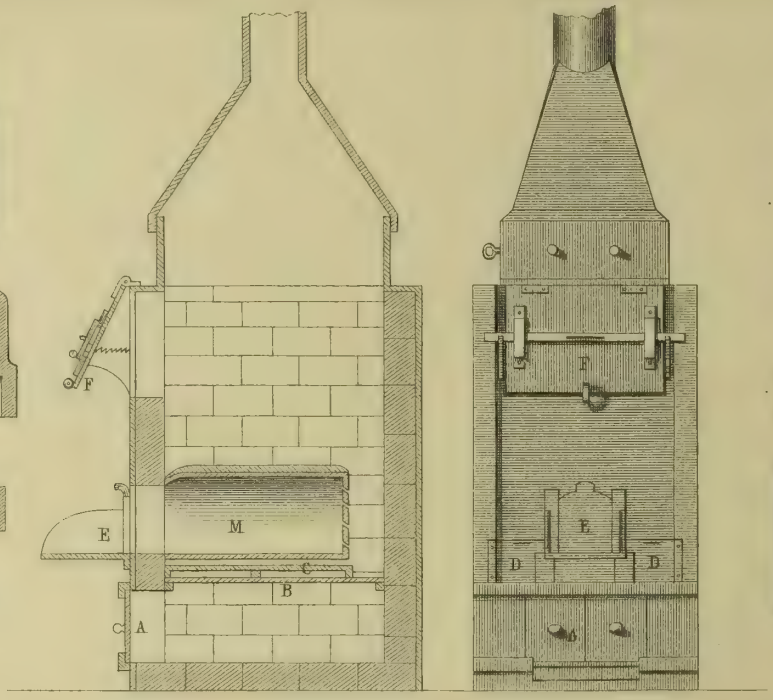


Fig. 2.

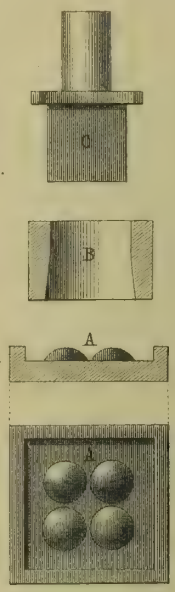


Fig. 3.

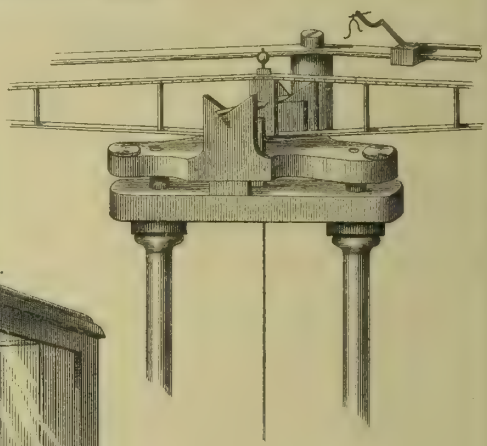
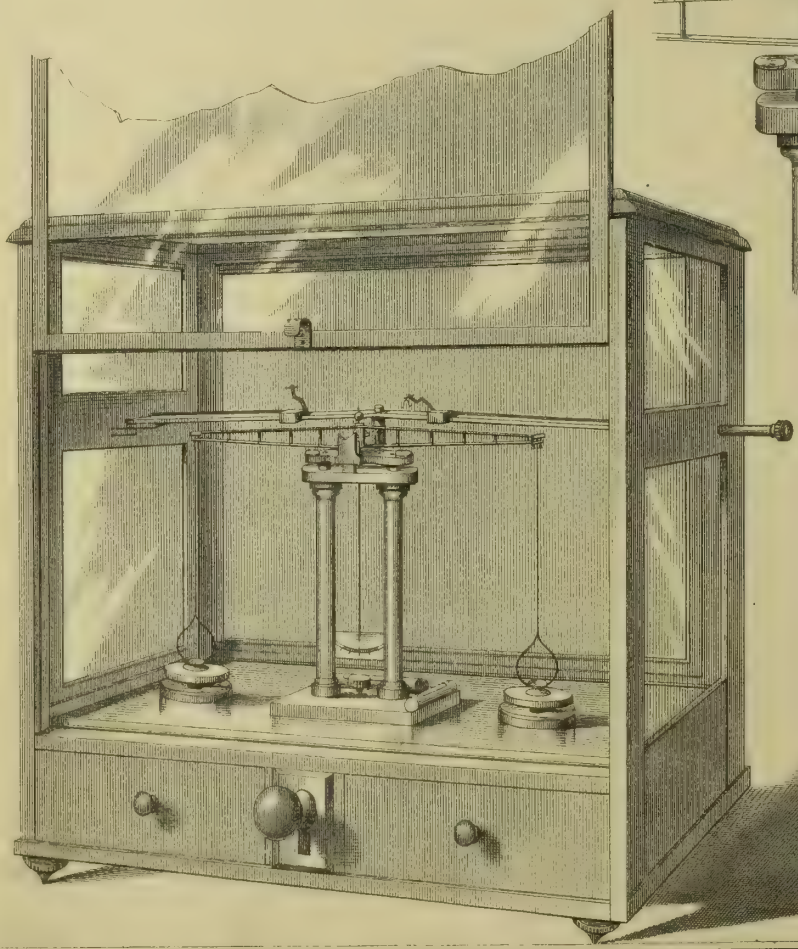


Fig. 4.





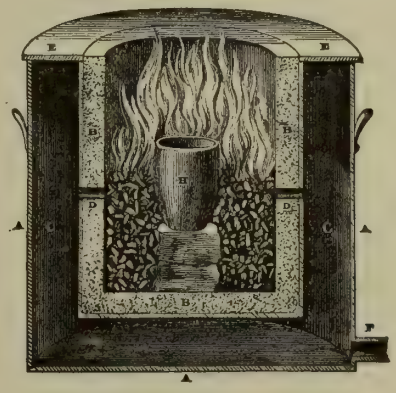
scale pans rest in stirrups of palladium, and can be removed by means of forceps. The supports at the centre and ends are shown on a large scale on the Plate. Each stirrup hangs from two steel points resting in agate cups, and the agate knife edge at the centre does not come in contact with the agate palates until after the supports have been removed from below the scale pans by means of the handle, moving in a vertical slot in front of the balance. As has already been described at page 96, two systems are employed for expressing the composition of gold and silver ingots, and the weights used in "weighing in" and "weighing out" the assays are usually so prepared that the results obtained directly represent the composition, rendering calculations unnecessary. Thus when reports of gold assays are required on the trade system, the weight of metal employed (varying from 5 to 16 grains), called the "assay pound," is divided into 24 parts, called carats, and each of these is subdivided in the manner shown by the table on page 95. If, however, assays are required on the millesimal system, the weight taken is called 1000, and in weighing the cornet after the completion of the assay subdivisions of this 1000 are employed. Those employed in reporting silver assays on the trade system are somewhat different.

The adjustment of the weight of the assay piece, so that the index of the balance should point to zero, would waste a considerable amount of time, and it is usual therefore to make a note of any slight divergence, not exceeding about three scale divisions (each of which represents the $\frac{1}{10000}$th part of the assay piece) on each side of zero, and to apply this correction in the final weighing. If the gold does not contain about $2\frac{1}{2}$ times its weight of silver it is necessary to add silver up to this amount, and the two metals are then wrapped up in a piece of sheet-lead, and placed on a tray divided into numbered compartments, which correspond to the positions of cupels in the muffle; the number of the compartment in which each assay is placed being noted with a view to its subsequent identification. This description of the preparation of the assay piece applies only to alloys, such, for instance, as those used in the coinage, and in which the next operation of fusion is not required, there being no earthy impurities present.

Fusion with Oxide of Lead.—Assuming, as before, that the ore to be assayed is gold quartz, it must first, as in all other cases, be reduced to a fine powder, by triturating in an iron mortar. This operation is much facilitated by heating the quartz to redness, and plunging it in cold water. Having pulverized a few thousand grains, it is usual to make at least two assays of the sample, to test the correctness of the result. For each of these weigh 500 or 1000 grains, according to the richness of the ore, and mix intimately on a clean surface of glass, or highly-glazed writing paper, with about the same weight of litharge or red lead, half the weight of dried carbonate of soda, and rather more than half of powdered charcoal. The precise quantities are not very important, but it is better that the carbonate of soda should be in excess than that it should fall short of the above proportion. PHILLIPS recommends the following proportion for the assay of a rock which does not contain an appreciable quantity of iron pyrites—600 grains of finely pulverized ore, 4000 grains of litharge or red lead intimately mixed with it, and from 15 to 20 grains of flour, starch, or finely powdered charcoal. The mixture is introduced into a Cornish or black-lead crucible (PHILLIPS, however, recommends ordinary French pots), which it should not more than two-thirds fill; it may then be covered with a thin layer of borax, and afterwards fixed solidly in the furnace by surrounding it with fuel.

Furnaces suitable for assaying are of various forms, and the required temperature may be obtained in them either by supplying an artificial blast of air by some blowing apparatus, or by connecting the furnace with a chimney sufficiently high to establish a strong natural draught. When the materials for its erection can be obtained the ordinary wind-furnace is to be preferred. This is represented

Fig. 30.

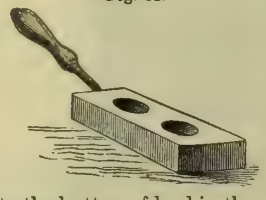


and fully described in connection with the assaying of copper ores, at page 570, vol. i., to which the reader is referred. For the travelling assayer, however, a portable apparatus is required, and in this respect SEFSTRÖM'S blast-furnace offers peculiar advantages. This consists of two cylinders of sheet-iron, placed one within the other, as represented in the annexed drawing, Fig. 30. A represents the outer cylinder, which answers the purpose perfectly well when not larger than a man's hat; and B the inner one, lined with a coating of fire-clay about 1 inch in thickness. Both cylinders are provided with a bottom, and are fixed together at the top, air-tight, by a horizontal hoop or flat ring of metal, E E, in such a way as to leave an equal space, C C, between their sides and bottoms. The interior cylinder, B B, is pierced at about the middle of its depth with eight holes, D D, which pass through the lining of fire-clay, and all point to the centre of the furnace, where the crucible, H, is placed on a piece of fire-brick, kept in its position by a little fire-clay, and surrounded with fuel. For a small furnace of this kind charcoal must be employed as fuel, and should be broken into

pieces about as large as a walnut. The air is blown into the opening, F, by means of a double-action bellows; or a simple rotating fan may be used. By this means the air is driven in a steady equable current through the holes, D D, into the cavity of the furnace. The heat which may thus be produced with a furnace having an internal diameter of not more than six inches, is so intense as to be capable of melting manganese, or several ounces of cast iron, with the greatest ease.

To proceed with the fusion. It has been stated that the mixture above-mentioned, when introduced into the crucible, should not fill more than two-thirds of its capacity. This precaution is necessary on account of the effervescence which will take place, owing to the displacement of the carbonic acid from the carbonate of soda by the silica, and the combination of the carbon with the oxygen of the litharge. The heat is continued till perfect fusion is effected, and towards the last the temperature is raised to bright redness, until no further effervescence occurs, and a clear liquid homogeneous slag is obtained. The crucible must then be immediately removed from the fire, otherwise the unreduced litharge would be liable to cut through the pot; and as dexterously and rapidly as possible, the slag, which constitutes the upper portion of the contents, is poured into one of the two hemispherical cavities of a cast-iron ingot-mould, Fig. 31, and then the lead, with adhering slag, into the other. If any particles of lead are found attached to the slag which is poured into the first cavity, they must be carefully separated by trituration and washing, and added to the button of lead in the other cavity. The latter is then taken out, and struck carefully on the side, on a bright anvil, with a hammer, to detach any portions of slag that may still adhere to it. Sometimes the crucible is broken to extract the button of lead, but this may be avoided by the method above described, if executed with sufficient dexterity. The whole of the gold, with any silver that may be present, remains in the lead, which is then subjected to the process of cupellation.

Fig. 31.



The proportion of oxide of lead to be used in the fusion will necessarily vary with the amount of oxidisable substances present; but this compound should in all cases be added in excess, since, if the slag retains any traces of an alkaline sulphide, it will retain a part of the gold. Phillips states that, for the assay of iron pyrites, about 30 parts of oxide of lead are necessary, whilst for mispickel, zinc blende, copper pyrites, grey cobalt, and sulphide of antimony, from fifteen to twenty-five times their weight only may be employed. When auriferous pyrites is the subject of examination, it must first be reduced to fine powder, and then roasted in a shallow dish of refractory clay, heated to low redness in a large muffle, until the odour of burning sulphur ceases to be evolved. As the sulphur burns away, the temperature is gradually raised to bright redness. The pyrites is thus converted into oxide of iron. Of this product 1000 grains or more may be taken, and mixed with 500 of dry carbonate of soda, 300 to 500 of litharge or red lead, and 5 per cent. of charcoal, or a corresponding quantity of granulated metallic lead without charcoal, and lastly, about 500 of dried borax. This mixture is heated, introduced into the crucible, and fused as for quartz or other common ores. The fuel should be either charcoal, coke, or anthracite. For small portable furnaces, such as Sefström's, charcoal is employed, but anthracite is found to be well adapted for the air-furnace, and is characterised by its power of producing an intense heat in a short time, over a space confined to a few inches above the bars.

The principal objection to this method of assay is the large amount of lead which is left for cupellation, since pure iron pyrites requires, when thus treated, $8\frac{1}{2}$ parts of lead, and sulphate of antimony and grey copper ore yield from 6 to 7 parts. This inconvenience, as well as the trouble of roasting, may be avoided by the cautious and gradual addition of nitrate of potassa, which effects the partial oxidation of the mineral, and enables the skilful assayer to procure a metallic button of almost any required weight. The nitre, however, if employed in excess, would determine the oxidation of all the metallic and combustible substances contained in the mineral, except the gold alone, which is never present in sufficient quantity to form a button. The exact amount of nitre to be added must depend on the nature and richness of the ore. As a general rule, it may be stated that $2\frac{1}{2}$ parts of nitre are sufficient to completely oxidize 1 part of iron pyrites, and that $1\frac{1}{2}$ and two-thirds their weight, in the cases of sulphide of antimony and galena respectively, are sufficient to produce the same effect on these ores.

Alloys of gold containing *tin* and *zinc* must likewise be fused, before cupellation, with nitrate of potassa, to oxidize these metals; and by adding about 16 parts of lead, when the mixture is quite melted, they are separated in the state of slag or scoria, leaving, as before, a button of lead containing the whole of the gold, which is now ready for being cupelled. But before describing this part of the assaying process, the method by scorification, which is often preferred to that of fusion with oxide of lead, will be briefly explained.

Method by Scorification.—Scorification, or, in other words, the conversion of the silica and other impurities into a scoria, is simply another method of fusion, in which, however, metallic lead, instead of its oxides, is employed; and the oxidation of the various substances to be removed is produced by the aid of atmospheric air, whilst the litharge necessary for the fusion of the earthy and silicious matters is formed by the oxidation of a portion of the metallic lead. For this operation, instead of a crucible, a shallow cup-like vessel, termed a *scorifier*, is employed. This vessel, the form of which is represented in

Fig. 32, should be made of refractory clay, and be as compact in structure as possible, in order to resist the corrosive action of melted litharge. The scorifier with its contents is heated in the muffle of an ordinary assay-furnace, and as many assays may be introduced at one time as there is room for in the muffle.

Fig. 32.



Fig. 2, Plate III., represents, in front elevation and vertical section, the form of furnace at present employed in the Royal Mint, which was arranged by Field, the late assay master, and which is convenient both for this purpose and for the subsequent operation of cupellation; the muffle used in it is shown at M. This last is an arched oven of fire-clay, the mouth of which is slightly contracted, and it is closed at the back; the closed extremity being pierced with a number of cylindrical holes in order to insure a free circulation of air through the interior. It is advisable that these holes slope outwards, as shown in the figure, in order to prevent any fuel from falling into the muffle. The top is roughed in order that it may be strengthened by a coating of fire-lute. This form is called the "Royal Mint" muffle, and is manufactured by the Plumbago Crucible Company. It rests on a plate of fire-clay, beneath which is an iron girder-plate, C, placed upon the fire-bars, B. The furnace is made of wrought iron about one-eighth of an inch thick, the whole being lined with fire-bricks, and the figures represent it to a scale of about three-fourths of an inch to the foot. It will be seen from them that the furnace is provided with five distinct openings, the lower one, A, in order to clear the ash pit; the two side ones, D D, to remove two fire-bars, to admit of the fuel being dropped into the ash pit; and the two, E and F, to charge the muffle and furnace respectively with cupels and fuel. By means of these perfect control is obtained over the fire, and any required course can be given with facility to the in-going current.

It may be added, convenient furnaces have been designed by Wiesnegg of Paris, Issem of Berlin, Griffin and Faulkner, suitable for making a few assays at a time, coal gas being employed as fuel. Watson, of the Sheffield assay office, has for some time employed a gas furnace capable of holding about 30 cupels at a time, the chief peculiarity of which is that the muffle is open to the air at both ends.

Before introducing the ore into the scorifier, it is reduced to powder, and a determined weight, about 50 grains, is intimately mixed with from 3 to 5 times its weight of granulated lead (the larger quantity being required for poor ores), and one-tenth its weight of borax; this having been placed in the scorifier is covered with from 150 to 200 grains of granulated lead, care being taken that the lead employed contains no silver. The scorifiers charged with this mixture are then placed in the muffle, and the door at the mouth being closed, they are strongly heated during a quarter of an hour. By this time the lead will be completely melted, and the mouth of the muffle is again opened. The scorifying process now proceeds in consequence of the current of heated air which passes through the muffle; in other words the lead is oxidized, and the foreign metals present, whether in combination with sulphur or oxygen, are attacked and dissolved in the litharge in proportion as this oxide is formed. At first the slags are frequently solid, but gradually become soft, and more and more liquid in proportion as the quantity of oxide of lead increases.

It is frequently desirable, when the surface has become covered with litharge, to introduce 15 grains of anthracite or charcoal, as by this means a portion of the lead is reduced to the metallic state, and by sinking through the mass of slag takes up any particles of precious metal which may be present. Towards the conclusion of the operation, the muffle is for a short time strongly heated to render the slag or scoria completely liquid. When a small iron rod, heated to redness and placed in the mixture, is found on being withdrawn to be covered with a slight film of scoria which runs off clean, the scorification is known to be sufficiently advanced. The scorifiers are then successively withdrawn from the muffle by means of tongs, and the contents are rapidly poured into circular ingot-moulds of the form represented in Fig. 31. When cold, the adherent litharge is detached from the button of lead by a few blows with a hammer. This button contains all the gold and silver which may have been present in the ore, and they are separated from the lead by cupellation.

When the material to be scorified is highly carbonaceous, such as the "sweep" or refuse constantly accumulating in the Mint, it is advisable to calcine previous to the addition of the lead, &c.

If the ore be poor the whole of the precious metals contained in a large quantity may be concentrated in one small button of lead by repeating the process on successive portions of ore mixed with the requisite amounts of lead, and introducing into each assay the button previously obtained. A final button containing all the precious metals from the several quantities of ore will thus be procured. The process may be repeated a third, fourth, or any number of times, till the button of lead last obtained becomes as rich in the precious metals as may be required. It is necessary, however, that a certain amount of lead be present, with a view to the next process, that of cupellation. In many cases as much as ten times the weight of the ore is employed, but the button may be reduced in size by a single operation to one-sixth or even to one-eighth of the original lead. Indeed, it is the highest recommendation of this process, as compared with the method by fusion with litharge, that however small may be the proportion of lead, the slags produced never contain any oxysulphides at the close of the operation, and therefore they seldom retain the slightest trace of either gold or silver. The process of scorification has therefore been justly characterized as one of the most exact methods that can be employed—simple, effective, and applicable to the assay of all kinds of auriferous and argentiferous ores, without exception.

Cupellation of the Assay.—The process of cupellation on the large scale has been already described. When applied to assaying the principle is the same; but in this case the whole of the melted litharge and other oxidized matters are removed by absorption into the cupel; whereas it has been shown that in operating on large quantities the cupel is soon saturated, and the greater part of the litharge and other oxides are allowed to run away, or are expelled by the current of air which causes the oxidation.

The cupels for assaying purposes are formed of the same material as those employed for refining on the large scale, and described at page 91; but they are necessarily much smaller, and are considerably simpler in their manufacture. They are made by pressing the moistened bone-earth into a mould of cast iron or gun metal, which varies in construction. Two forms at present in use in the Royal Mint are shown in Figs. 1 and 3 on Plate III. one-half their actual size. In the first of these, after the space in the piece of metal, A, has been rather more than filled with bone-ash, the guide, B, is placed over it. The plunger, C, having been introduced into this guide, the whole is placed under a common lever in press, by which means the bone-ash is compressed into the form shown in Figs. 33 and 34, and Fig. 1. on the Plate. Formerly the plunger was struck several times with a hammer in order to give the required compression. It is desirable to give a slight twisting motion to the plunger on removing it. The second form of mould, shown in Fig. 3, has been introduced in order to diminish the labour of the furnace manipulation. It will be seen that each cupel is square, and is provided with four depressions. Each of these is, however, rather smaller than the one already described, the amount of metal operated upon in the two cases being about 7·5 and 16 grains respectively. The square cylindrical piece, B, having been placed on the plate, A, is filled with bone-ash, and with the plunger, C, is introduced as before into the press, the cupel when formed being five-eighths of an inch deep, square, and slightly tapered towards the bottom. The cupels when formed should be kept in a dry place for several months, as it is found that when any method of hastily drying them is adopted they almost invariably crack when introduced into the muffle, and cause the assays to spurt.

Fig. 33.

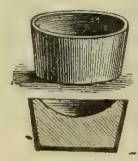


Fig. 34.

Cupellation, like the process last described, is performed in a muffle furnace, as shown at Fig. 2, Plate III. At the time of lighting the furnace, the requisite cupels are successively introduced into the muffle by a pair of light tongs of the form represented in Fig. 35, the floor of the muffle being covered with a thin layer of bone-ash before the introduction of the cupels. In the furnaces of the Mint the number of assays that can be made at one time is forty-five when the large "assay pound" is used, and seventy-two with the small one, and it is usual to introduce an additional row of cupels when possible, to be employed in case of accident. The temperature of the muffle having been raised to an orange red heat, the assay pieces, either in the form of buttons mixed with lead as obtained by scorification, or as samples of alloy wrapped in lead-foil, as already described, are successively introduced into the cupels, care being taken that they are so arranged as to avoid any possibility of confusion on their subsequent removal. It is advisable that while the muffle is being thus "charged" the door should be partially closed by means of a hot firebrick, in order to check as much as possible the chilling of the cupels which are near to it. The requisite amount of lead (which will be presently given) may be all introduced as a wrapper of the assay piece. Of course when the alloy for assay consists of a button obtained by a previous process of fusion or scorification, this addition of lead is unnecessary, as a sufficient amount is already contained in the button.

Fig. 35.



By the previous process of fusion with litharge, or that of scorification, if deemed preferable, the earthy impurities have been removed in the form of slag or scoria, and nothing now remains but the gold, or a mixture of gold and silver, in combination with the lead and any other metals that may be present. The process of cupellation, as previously stated, consists in the oxidation of the lead and other oxidizable metals, and their absorption by the cupel. It is, in fact, a condition essential to the success of the assaying process that the whole of the oxides should be imbibed, and thus removed. But the power of absorption in a cupel varies according to its texture, and the care with which the material has been prepared. On an average, it may be calculated that it will absorb about its own weight of fused litharge. This, though not strictly correct, will help to guide the experimenter, as regards the amount of lead which ought to be mixed with the assay. It is evident, on the one hand, that this must not exceed the absorptive power of the cupel. On the other hand, the actual amount within this limit must depend on the nature of the alloy upon which the cupellation is to be performed; but supposing that the subject of assay is an alloy of gold and copper, the following table will give the quantity of lead required for the separation of the copper. In treating an alloy of gold and silver with copper, the quantity of lead may be somewhat diminished; but in cupelling an alloy of copper with gold alone, a small excess of lead is not injurious, as, in consequence of the gold not being volatile, like silver, the heat can be raised and sustained for any length of time, so as to oxidize the last portions of lead. In this table, which shows the proportion of lead recommended by D'Arcet, the first and second columns express respectively the quantity of gold and of copper in 1000 parts of the alloy, and the third column gives the number of parts of lead required for one part of the alloy according to its composition:—

Alloy.		
Quantity of Gold.	Quantity of Copper.	Proportion of Lead required.
1000	0	1 part
900	100	10 "
800	200	16 "
700	300	22 "
600	400	24 "
500	500	26 "
400 to 0	600 to 1000	34 "

KANDELHARDT gives somewhat different proportions, as is shown in the following table:—

Alloy.		
Quantity of Gold.	Quantity of Copper.	Proportion of Lead required.
1000	0	8
980 — 920	20 — 80	12
920 — 875	80 — 125	16
875 — 750	125 — 250	20
750 — 600	250 — 400	24
600 — 350	400 — 650	28
350 — 0	650 — 1000	32

It must be observed that the numbers in the third column indicate multiples of one part of the alloy. It may appear surprising that, at and below the point at which the alloy contains 600 parts of copper, the same proportion of lead is required, whatever may be the proportion of the copper. This fact, however, has been fully verified by experience. It requires, in short, as much lead to remove the copper from an alloy containing 600 parts of that metal, as it would to carry off a quantity of copper equal to the weight of the copper and gold together. It should be added, that when the assayer knows approximately the composition of the alloy, he should insure the presence of about two and a half times as much silver as gold, which is not only useful in the cupellation, to guard against the loss of gold, but is necessary, as already stated, for the subsequent operation of parting.

The assays having been placed in the cupels, the opening into the muffle should be loosely closed by an additional piece of hot fire-brick placed above the first, or by pieces of charcoal. After a short interval all the assay pieces will be melted, and in each cupel will be seen a round mass of molten metal, on the surface of which appear bright patches of litharge; these are produced by the oxide of lead which is constantly forming, and passing off from the centre to the edges of the assay, where it meets with and sinks into the porous matter of the cupel, leaving always a new surface exposed to the current of air which is carried through the muffle. At the same time there rises, and passes through the openings of the muffle, a white vapour which is caused by the volatilization of a portion of lead. When this vapour is very thin and rises with great rapidity, it is an indication that the heat is too great, and part of the draught must be stopped; on the other hand, when it is thick and heavy, and hangs sluggishly over and around the cupel, the temperature is too low, and the draught must be increased.

According to MAKINS, the draught should be so adjusted that no appearance of fumes is manifest, and thus the cupel should be found to have increased in weight by the weight of lead together with its equivalent of oxygen.

As soon as the greater part of the lead has been thus converted into litharge and absorbed, the remaining bead of rich alloy suddenly becomes opaque and glowing, and is traversed by iridescent bands produced by the extremely thin films of fluid litharge resulting from the last traces of lead. This is a sign that the process is on the point of completion, and means must now be taken to increase the heat of the furnace for a short time, so as to insure the expulsion of the last remaining portions of lead. But if silver be present in the assay, and if it be desired to estimate also the amount of that metal, the increase of temperature towards the end of the process must be of short duration, otherwise a considerable portion of the silver would soon volatilize. Immediately after the disappearance of these bands the globule becomes steady, after which the peculiar action known as "brightening" takes place, when the metal is observed to emit a brilliant flash of light, and it immediately solidifies. If the cupellation has been well performed, the gold or the mixture of the two precious metals is now in a state of almost chemical purity.

When the cupellation is terminated, the mouth of the muffle ought to be closed, and the whole allowed to cool until the buttons become solid; or, when only a few assays are performed at a time, the cupels containing the buttons of pure metal may be drawn to the front of the muffle, and allowed to cool slowly. This refrigeration must not be too rapid, otherwise there may be very sensible loss by "spitting, sprouting, or vegetation"—an effect, however, only produced when a large proportion of silver is present, and which has been already explained in connection with the process of cupellation on the large scale. To insure gradual cooling, it is occasionally convenient to invert over the cupel containing the bead another heated cupel. Some assayers remove the cupels from the furnace while the metal is in a molten state, but the practice cannot be recommended, for in addition to the danger of upsetting a cupel and the "spitting" of the assay, the buttons are found to be more malleable when cooled gradually.

The button is detached from the cupel after cooling by a pair of steel forceps, cleaned with a brush formed of stiff bristles, and flatted as presently described. If the process has been successful the button should be round and bright upon its upper surface, but somewhat rough or crystalline on the part by which it was attached to the cupel, from which it ought to be removed without difficulty.

The presence of iron, tin, nickel, or zinc in the alloy under assay materially interferes with the success of the operation, as these metals will not pass into the cupel by the aid even of a large quantity of lead; but from their rapid oxidation will either volatilize, or their oxides will accumulate on the surface as a sort of slag, in which particles of precious metal may be entangled. In this case the assay

becomes what is technically termed *foul*, the cupel not being able to absorb the metallic oxides as they are formed. To obviate this evil, the preliminary process of scorification should be resorted to, when the presence in the alloy of any of the above metals is known or suspected. A convenient weight of native gold or rich alloy to operate upon is 10 to 15 grains.

Bismuth might be used as a substitute for lead in cupellation, 2 parts of it being nearly equivalent to 3 of lead; but its higher price prevents its general use for this purpose. The lead employed must be in all cases entirely free from silver, being such as has been derived from pure litharge, otherwise it would be quite impossible to estimate the true composition of the alloy. The assay of gold furnishes results which are more accurate than those obtained in the cupellation of silver; the loss of gold by volatilization is very much smaller, and scarcely any of the metal is carried into the cupel by the lead.

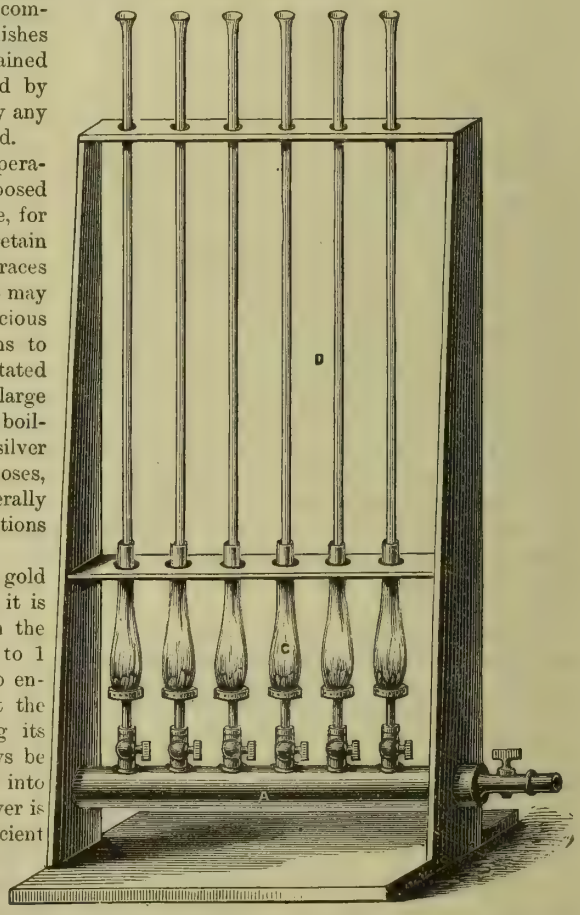
Parting of the Assay.—After the preceding operations, the button of alloy which remains is composed of gold and silver, not, indeed, absolutely pure, for whatever precautions may be used it will still retain a small quantity of lead, and frequently also traces of copper. For practical purposes, however, it may be regarded as a pure alloy of the two precious metals, and in this view it now only remains to separate the gold from the silver. It has been stated that on the Continent this is effected on the large scale by means of sulphuric acid, which at its boiling point possesses the property of dissolving silver without acting upon gold. For analytical purposes, however, nitric acid is preferred, and is generally employed in this country, even for refining operations on the large scale.

It has been stated, also, that when silver and gold are intimately mixed together, as in an alloy, it is necessary that the silver should be present in the proportion of at least $2\frac{1}{2}$ parts of that metal to 1 part of gold, otherwise its particles will be so enveloped and protected by those of gold that the nitric acid will be prevented from exercising its solvent action upon them. Care should always be taken before the introduction of the assay piece into the furnace that the requisite proportion of silver is present; and if this be the case, it will be sufficient at once to subject it to the action of the acid. But if the silver be present in a less or much greater proportion, then, as a preliminary step to the operation of parting, the alloy must be brought to the proper standard, either by the addition of the necessary quantity of pure silver, or by adding more gold, as the case may be; for if the proportion of silver exceed 3 parts, the gold will be precipitated by the acid as a dark powder, instead of retaining the compact form; and thus the accuracy of the estimation of the amount of gold present will be impaired.

It is hardly necessary to add that the amount of silver requisite can only be determined when the approximate assay is known. This may be determined by a wet analysis, a rough assay, or by the touchstone; or experienced assayers are able to determine with sufficient accuracy by observing the colour and the facility with which the metal can be cut with shears.

The button is now flatted by hammering on an anvil, three strokes being so given as that the first shall extend it to about the size of a sixpence, and the other two reduce the thickness still further at two opposite edges, in order to facilitate introduction afterwards into the laminating mill. These flatted buttons are generally annealed before rolling; but the practice is not universal, and, although the labour is greater, they are at times passed directly through the rollers. By this operation the thickness is reduced to about one-eightieth of an inch, and, when all the laminæ have been placed in slits on a wrought-iron tray, they are introduced into the muffle and annealed. The operation renders them sufficiently flexible to allow of their being twisted into a small spiral *cornet*, by rolling between the finger and thumb, or by means of a pair of round-nosed pliers.

Fig. 36.



The method of performing the next operation, the *parting* of the assay, has been very materially altered during the last few years. Formerly each assay was boiled separately in strong nitric acid, contained in a

small glass flask, called a parting flask, and this plan is still adopted when assaying is not practised on a large scale, but when, as in the Royal Mint, there are large numbers of assays constantly required to be made, an apparatus formed of platinum, and introduced by Messrs. Johnson, Matthey, & Co., is now very generally employed. It may be useful, however, to describe both these methods. Fig. 36 represents a convenient apparatus for boiling six cornets separately. The large tube, A, is connected with the gas supply, and from it rise a number of small rose Bunsen burners. On these rest the parting flasks, C, into each of which is introduced from 2 to 3 ozs. of nitric acid of spec. grav. 1·26. The long tubes, D, dipping into the mouths of the flasks,

Fig. 37.

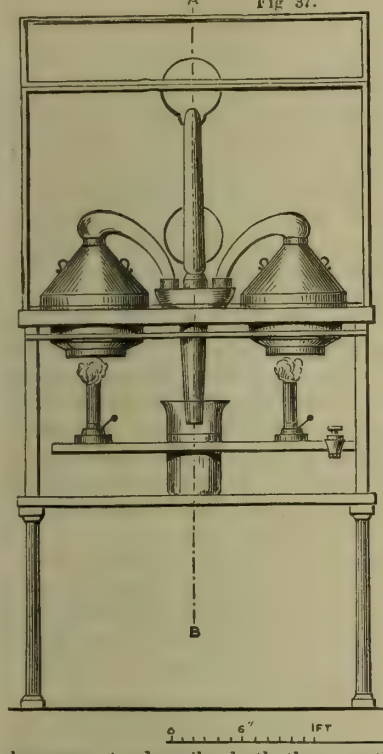


Fig. 38.

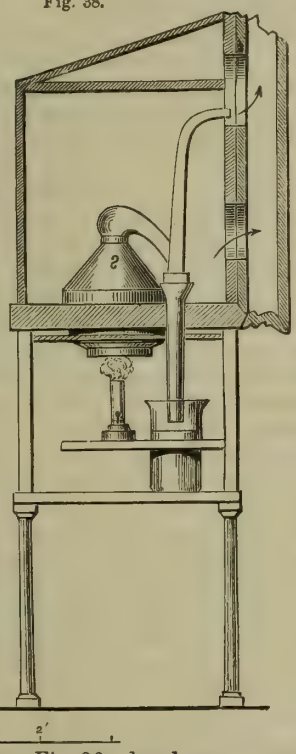
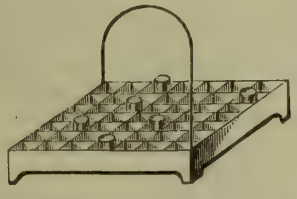


Fig. 39.



Fig. 40.



are intended to condense as far as possible the acid vapours, the condensed liquid running back into the flasks. In cases where a large number are in action at once they should be connected with a flue to carry off these vapours. The acid should continue to boil for from three to five minutes after the glasses have cleared of fumes; the acid is then poured off, the cornets washed with hot distilled water, and again boiled for from fifteen to twenty minutes in nitric acid of about spec. grav. 1·30. As the ebullition is at times very violent, and the cornet extremely fragile, owing to its spongy nature, it is generally recommended that a piece of charcoal be introduced into each flask. This, however, is objectionable, for it may cause the formation of nitrous acid, which by absorption in the acid will even dissolve portions of the metal. This source of error is completely eliminated by using instead small balls of porous earthenware, as recommended by Field.

The last acid having been poured off, the flask is completely filled with distilled water, and a small, smoothly-finished, porous clay crucible is placed over the mouth of it. The two vessels, thus adjusted, are then inverted, so as to allow the cornet to fall gently through the water into the crucible, and by a dexterous movement of the hand the flask is withdrawn, in such a manner as to prevent the overflow of any liquid from the little crucible. The water is now carefully decanted and the silver which it contains is subsequently extracted; the crucible containing the cornet is heated to redness in the muffle. Under this final heating it is not fused, but shrinks in bulk, loses its brown appearance, and assumes the peculiar colour and lustre of gold; while at the same time it is rendered more compact, less brittle and fragile, and when cold, can be removed by a pair of forceps to the scales, in which it is weighed with the same precision and care as the original alloy.

The second method, however, of parting above referred to is far preferable where large numbers of assays are frequently made. The apparatus required is formed entirely of platinum, the joints being made with gold. It is represented to scale in front elevation and section in Figs. 37 and 38, and consists of two boilers furnished with movable covers and condensing tubes, which rest in water troughs when the apparatus is in action. The acid vapour is partly condensed, and passes into a suitable receptacle, the remaining fumes passing into a flue. The two boilings are performed one in each boiler. Each strip of metal, after being coiled into a cornet, is placed in a small platinum cup, as shown in Fig. 39; and the requisite number of these is introduced into a platinum tray, shown in Fig. 40, the bottom of which is perforated, and which is divided into a number of compartments. The whole is then placed in the first acid, and boiled for about fifteen minutes. The tray is then removed, dipped into distilled water, and placed in the second stronger acid for about twenty-five minutes. On its removal the

tray and its contents are placed in the muffle and annealed at a dull red heat, care being taken that the temperature does not rise too high, as the cornets are liable to adhere to the platinum cups, which it must be admitted is a slight objection to the use of this apparatus; and the only other fault which can be found with it is the impossibility of determining whether any, and if so which assay pieces contain platinum or palladium, a fact which was immediately decided in the old method of parting in separate vessels by the colour imparted to the acid. But when a number of assays is made on metal of fairly uniform composition, as in coinage operations, the apparatus is invaluable, and compared with its advantages these faults are unimportant.

The weight of the cornet will indicate very nearly the amount of gold in the alloy if the assay has been properly conducted, but not with absolute exactness. Even when every precaution has been used, the gold contained in the cornet is never chemically pure; it still retains a very small quantity of lead and of silver, and frequently also traces of copper, in consequence of which the weight of the cornet may exceed by $\frac{1}{2000}$th part the true result; and when it is considered that in assaying alloys the quantity taken is often not more than 7 or 8 grains, it will be seen that even this small error might lead to serious disappointment in estimating the proportion of gold in large masses of bullion. To ascertain the amount of the error, and thus arrive at a perfectly correct estimate, it is usual to assay, simultaneously with the alloys, a number (generally three) of what are termed *proofs*, consisting of weighed portions of perfectly pure gold, approximately equal in amount to that present in the assay pieces. The cornets obtained from these proof-assays are weighed, and the excess or deficiency in weight over that of the gold which was introduced indicates the amount of the correction which it becomes necessary to apply to the other assays. This correction is liable to variation, according to the temperature of the furnace and other causes; but it usually ranges from 0·2 to 0·5 in 1000. It may be observed that it is not essential to employ *absolutely* pure gold, provided the difference from purity be known. Thus the corrections to be applied to a gold assay will be readily understood from the following formula, where (1000 representing the weight of alloy originally taken)—

p is the weight of the piece of gold finally obtained.

x, the amount of gold in the alloy, expressed in thousandths.

a, the weight of gold (almost absolutely pure) taken as a check, which approximately equals x.

b, loss or gain in weight experienced by a during the process of assay.

k, variation of "check gold" from absolute purity, expressed in thousandths.

The actual amount of fine gold in the check-piece—

$$= a\left(1 - \frac{k}{1000}\right),$$

and the corrected weight of the cornet will be—

$$x = p - \frac{ak}{1000} \pm b$$

b being added or subtracted according as it is a loss or gain. If a be assumed to be equal to x, this equation becomes—

$$x = \frac{p \pm b}{1 + \frac{k}{1000}}$$

The actual amount of metal retained, called *surcharge*, is greatly influenced by the amount of copper present in the alloy under examination, and varies considerably with the heat of the furnace and other circumstances. In an alloy rich in gold, and which therefore required only a small quantity of lead, the surcharge is slight; when, however, a large quantity of copper is present the surcharge becomes negative, in consequence of the absorption of gold by the cupel; and for alloys containing 68 or 70 per cent. of gold the surcharge is zero. Rossler has shown that the gold lost in the cupellation process increases with the amount of lead used, and decreases as the silver present is increased: and these conclusions are confirmed by the results of experiments recently made in the Royal Mint. He also considers that in general the gold lost is greater in amount than the silver retained by the cornet.

Parting Assays.—It is frequently necessary to determine not only the amount of gold *or* silver contained in a given alloy, but also the amount of each of these precious metals present in the same sample; the assays made with a view to obtain this information are termed "parting assays."

If the quantity of silver in the alloy submitted to the operation of parting be more than three times that of gold, the separation may still be effected by nitric acid, but the gold will be left in a state of powder. It may, however, be washed, ignited, and weighed in the manner described in connection with the quantitative estimation of gold by the wet method, and in the process of parting with sulphuric acid on the large scale. Should the amount of silver be but small compared with the gold, and the assayer wish to avoid the trouble of inquartation, that is, the adding of the requisite proportion of silver, the alloy may at once be subjected to the action of aqua regia, when the gold will be dissolved, and the silver will be thrown down as an insoluble chloride. The clear solution containing the gold is then decanted, and when the excess of acid has been expelled by evaporation, the gold can be precipitated, as already described, by sulphate of iron.

The determination of the amount of silver contained in gold by the dry method of assay is a somewhat complex operation. One or two gold assays in the ordinary way are made, and at the same time two more assay pieces are passed through the furnace, but without the addition of silver. By this means all the oxidizable metals are removed in both cases, and the difference in weight between one of the cornets resulting from the ordinary assay, and

the button of mixed gold and silver as drawn direct from the furnace, must be due to silver originally present in the alloy.

The silver contained in the solution of its nitrate, resulting from the common process of parting, may readily be recovered by adding an excess of chloride of sodium, which will throw down the whole of the silver as white insoluble chloride. This precipitate, which speedily becomes slate-coloured on exposure to light, is collected and put into a vessel containing water acidulated with hydrochloric acid; some zinc or iron is introduced, and the silver is rapidly restored to its metallic state, in the form of a dark-grey powder.

The supernatant liquid having been decanted, this fine metal is washed with dilute hydrochloric or sulphuric acid in order to remove traces of iron or zinc, but as the removal of the former of these metals may be effected more perfectly, it is now always used in preference to the latter; after washing with water, and drying, the silver is fused in a crucible with the addition of a little carbonate of soda or nitre, and cast into bars.

Physiological Effects, &c.—Gold, says Pereira, like other metals, has been frequently supposed to be inert while it retains its metallic condition, but in this, as well as in some other instances, the accuracy of the assumption has been denied. Both Chrestien and Niel, as well as other writers, assert that finely-divided metallic gold—*pulvis auri*—produces the same constitutional effects as those caused by the various preparations of this metal, but in a milder degree, while it excites little or no irritation. It is said to promote the secretions of the skin, kidneys, and salivary glands.

It has been employed as an antivenereal and anti-scrofulous remedy by Chrestien, Niel, and others, with considerable success. It is said to be preferable to the other preparations of this metal in delicate and nervous subjects, females and infants. Gold-leaf—*aurum foliatum* seu *lamellatum*—is used by dentists for filling decayed teeth, and was formerly employed by apothecaries for covering pills—*ad inaurandas* seu *obducendas pilulas*. Silver-leaf now takes its place. It has been administered internally in doses of from a quarter of a grain to a grain three or four times a day. Chrestien used it by way of friction on the tongue and gums. Niel employed it endermically—that is, applied it to the skin deprived of the epidermis—in the form of ointment composed of 1 grain of gold and 30 grains of lard.

Teroxide of gold is sometimes used internally, in venereal and scrofulous diseases, in doses of from one-tenth of a grain to a grain, made into the form of pills with mezereum.

The terchloride of gold, the preparation of which is described at page 109, acts, according to Orfila, as a corrosive when introduced into the stomach of animals, but with less energy than the chloride of mercury, and destroys them by the inflammation of the coats of the alimentary canal which it sets up.

On man its effects are analogous to those of chloride of mercury. In *small doses* it acts, according to Chrestien, more energetically as a stimulant, though less powerfully as a sialogogue, than corrosive sublimate. It promotes the secretions of the skin, the salivary glands, and the kidneys. Taken to the extent of one-tenth of a grain daily, it has occasioned violent fever. Cullerier has seen one-fifteenth of a grain excite, at the second dose, gastric irritation, dryness of the tongue, redness of the throat, colic, and diarrhœa. When it promotes the secretion of saliva, it does not, as mercury, affect the teeth and gums. Magendie has seen violent gastritis, accompanied by nervous symptoms—cramps and pains in the limbs, agitation and loss of sleep—and afterwards great heat of skin and obstinate sleeplessness. In *large doses*, it would probably occasion symptoms similar to those produced by the use of poisonous doses of chloride of mercury.

It has been employed, with variable success, as a substitute for mercury in the secondary symptoms of syphilis. A more extended experience is, however, necessary to enable one to speak of its remedial powers with confidence. In the hands of Chrestien, Niel, Cullerier, Legrand, and others, it has proved most successful.

It has also been used in scrofulous affections, bronchocele, chronic skin diseases, scirrhous tumours, &c. Duportal cured with it a case of obstinate ulceration of the face, regarded by him as cancerous, and which had resisted all the ordinary methods.

Legrand has used terchloride of gold, acidified with nitric acid, as a caustic in syphilitic, scrofulous, and scorbutic ulcers, cancerous growths, and ulcerations of the neck of the uterus.

Internally, it has been given in doses of one-twentieth of a grain, made into pills with starch. But as organic matters decompose it, it is better to use it in distilled water, or to apply it by friction to the mouth, in quantities of from one-sixteenth to one-sixth of a grain.

The whites and yolks of eggs, milk, and a mixture of wheat-flour, oatmeal, or barley, and water, are, as in the case of chloride of mercury, antidotes for an overdose of this auric compound.

It is surprising that the above are so little used in medicine. Surely, if physicians would only daily experiment on the action of the different metals and their compounds upon the system, they might soon discover some very valuable specifics.

Statistics.—Gold and silver are frequently confounded in statistical returns under the common designation of the *precious metals;* and even where the two are classed separately, it is still desirable to place them in juxtaposition, since much of the interest attached to the subject is derived from the relation which they bear to each other. In stating the most important facts connected with the statistics of gold most of the corresponding figures relating to silver will also be given, which will not only save the repetition of a number of tables nearly similar, but will furnish the reader with a clearer and more satisfactory view of the subject, than if the returns

relating to each of the metals were tabulated separately in different parts of the work.

Much interesting information relating to the history and statistics of the precious metals is given in a work which was published by JACOB in 1831, in which he takes up the subject at the earliest period, and continues it to the year above-mentioned. JACOB shows that, in the days of Roman supremacy, the greater part of the wealth of the world continued to flow into Rome, up to the time of AUGUSTUS, when the production of gold from the Roman mines in Illyria and Spain suddenly ceased; and for a long period the world received no new accessions of metallic wealth. With much labour and research he constructed a table showing the rate of diminution to which the enormous wealth of the Augustan period was subject; and though it includes both gold and silver under one head, while at the same time its accuracy cannot be implicitly relied on, still it is sufficiently correct and instructive to merit a place in these pages:—

QUANTITY OF GOLD AND SILVER IN THE ROMAN EMPIRE.

Year.	
14	£358,000,000
50	322,200,000
86	287,980,000
122	259,182,000
158	233,263,800
194	209 937,420
230	181,943,678
266	163,749,311
302	147,374,380
338	132,636,942
374	119,373,248
410	107,435,924
446	96 692,332
482	87,033,099
518	78,229,700
554	70,406,730
590	63,364,057
626	57,027,652
662	51,324,887
698	46,192,399
734	41,573,160
770	37,415,840
806	33,674,256

From the decline and fall of the Roman empire the portion of gold added to that already obtained was for many centuries not more than sufficient to supply the annual waste by wear and loss; and except the mines of Hungary and Sweden, which do not appear to have been worked before the eighth or ninth century, no important new sources of gold were opened until the discovery of America by COLUMBUS in 1492. This event was followed in the course of the next century by a considerable influx of the precious metals into Europe; yet a very superficial inquiry will suffice to show that the actual amounts which were imported from Mexico and South America have been greatly exaggerated in the public mind, and sink into very humble figures when compared with the enormous treasures obtained from California and Australia. From 1492 to 1500 America, according to HUMBOLDT, furnished to Europe, in gold and silver, not more than £52,000 sterling, and the entire annual amount of gold and silver obtained from America during the sixteenth century was only about half a million sterling; whereas during the last twenty years the value of *gold alone* exported from California and Victoria has averaged about seventeen millions per annum. The celebrated *El Dorados* of the sixteenth century sink therefore into utter insignificance, compared with the recently-developed auriferous regions.

It is true that with the discovery of the Brazil mines and other sources the import of the precious metals from America continued steadily to increase; and from 1600 to 1700, during which period Europe obtained its supply of gold almost exclusively from the New World, the mines of the latter were estimated to have produced an amount of gold and silver equivalent to £337,500,000 sterling, or upwards of £3,000,000 per annum. In consequence of this continued importation, the value of the coined money in Europe in 1699 has been estimated at £297,000,000 sterling. During the eighteenth century the supply of the precious metals was still chiefly derived from America. The annual produce of the mines of that quarter of the globe at the commencement of the present century was estimated by HUMBOLDT at £8,700,000 sterling; and that derived from the European mines of Hungary, Saxony, &c., and those of Northern Asia, was valued by him at £1,000,000 sterling more, raising the total produce at that period, exclusive of Africa, to £9,700,000 sterling. The *quantity* of gold produced in America was to the *quantity* of silver as 1 to 46; in Europe as 1 to 40; and the *values* of equal quantities of gold and silver were then in the proportion of 15 to 1, so that the aggregate value of the gold to that of the silver was nearly 1 : 3; or, in other words, the annual amount of *gold alone* produced at the beginning of the present century was worth about £3,200,000 sterling.

From 1800 to 1810 the yield of the American mines continued still to increase, and in conjunction with that of the European and Russian mines is supposed to have amounted in the latter year to upwards of £11,000,000 sterling, in gold and silver. But in that year began the contest which resulted in the dissolution of the connection between Spain and her American colonies, causing the abandonment of several of the mines, and a consequent decline in the production of the precious metals to such an extent that, according to JACOB, the total average yield of the American mines, inclusive of Brazil, during the twenty years ending with 1829, might be estimated at little more than £4,000,000 a year, being less than half their produce in 1800. Some years later, however, they again began to increase; and this, in conjunction with the subsequent extraordinary development of the Russian mines, raised the entire amount of gold and silver produced from all the *known* auriferous localities throughout the world, *before the discovery of California and Australia*, to upwards of £12,000,000 per annum, the value of the gold to that of the silver being nearly as 5 : 6. This will appear from the following table, prepared by BIRKMYRE, showing, by approximate calculation, the annual produce of fine gold and silver for 1846 and 1850; the first being two years before the discovery of the rich deposits of gold in California, the latter two years after the discovery:—

Countries.	1846.			1850.		
	Gold.	Silver.	Total.	Gold.	Silver.	Total.
	£	£	£	£	£	£
California,	—	—	—	12,000,000	62,088	12,062,088
United States,	237,336	1,864	239,200	115,430	11,444	126,874
Mexico,	249,753	3,457,020	3,706,773	382,901	5,383,333	5,766,234
New Granada,	252,407	42,929	295,336	252,407	42,929	295,336
Peru,	96,241	1,000,583	1,096,824	96,241	1,000,583	1,096,824
Bolivia,	60,337	460,191	520,548	60,357	460,191	520,548
Chili,	145,585	297,029	442,614	145,585	297,029	442,614
Brazil,	259,871	2,003	261,874	289,068	2,227	291,295
Total of North and South America,	1,301,560	5,261,619	6,563,179	13,341,989	7,259,824	20,601,813
Russia,	3,414,427	167,831	3,582,258	4,175,860	171,817	4,347,477
Norway,	—	32,346	32,346	—	35,607	35,607
North Germany,	357	138,022	138,379	357	138,022	138,379
Saxony,	—	198,200	198,200	—	198,200	198,200
Austria,	282,750	282,654	565,404	288,708	286,971	575,679
Piedmont,	17,841	7,444	25,285	17,841	7,444	25,285
Spain,	2,498	227,499	229,997	2,498	440,210	442,708
United Kingdom,	—	109,989	109,989	—	160,000	160,000
Africa,	203,900	1,056	204,956	203,900	1,056	204,956
Borneo,	305,900	1,584	307,484	305,850	1,584	307,484
Ava,	100,000	517	100,517	100,000	517	100,517
Malacca,	72,240	374	72,614	72,240	374	72,614
Sumatra,	63,719	330	64,049	63,719	330	64,049
Annam or Tonquin,	30,585	53,460	84,045	30,585	53,460	84,045
Various countries,	50,975	33,000	83,975	50,975	33,000	83,975
Total of Europe, Africa, and Asia,	4,545,192	1,254,306	5,799,498	5,312,533	1,528,592	6,840,975
Total of North and South America,	1,301,560	5,261,619	6,563,179	13,341,989	7,259,824	20,601,813
Total,	5,846,752	6,515,925	12,362,677	18,654,522	8,788,416	27,442,788

The various countries are exclusive of China and Japan, which produce large quantities of gold and silver, the amount of which is quite unknown to Europeans.

BIRKMYRE estimates the produce of California alone in 1850 at £12,000,000—a figure so high that, notwithstanding the importance attached by MACCULLOCH to his calculations, seems to have far exceeded the truth. The following table is chiefly extracted from the *Economist* newspaper, which has the credit of deriving its statistical information from the highest official sources:—

Year.	Total Value of Gold Exported in each Year from				
	New South Wales.	Victoria.	Australia (All).	Production of Russia.	California.
1861,	£2,012,000	£9,081,000	£11,871,000	£2,980,000	£8,358,300
1862,	2,978,000	7,611,000	12,213,000	2,990,000	8,745,600
1863,	2,371,000	7,691,000	12,676,000	2,988,000	9,466,900
1864,	2,987,000	7,239,000	12,452,000	2,862,000	11,652,000
1865,	2,775,000	7,004,000	12,226,000	3,227,000	9,309,900
1866,	3,350,000	6,878,000	13,355,000	3,397,000	9,116,400
1867,	2,596,000	6,412,000	11,933,000	3,377,000	8,563,600
1868,	2,165,000	8,356,000	13,708,000	3,503,000	7,283,100
1869,	2,778,000	7,497,000	13,214,000	3,617,000	7,679,400
1870,	—	—	9,000,000	3,837,000	6,777,300
1871,	—	—	9,500,000	3,600,000	3,545,200
1872,	—	—	5,983,000	4,771,000	3,960,000
1873,	—	—	9,444,000	4,500,000	3,540,000
1874,	—	—	6,720,000	4,036,760	4,747,000

Annexed are a number of tables relating to the production of gold and its application, which, it is hoped, will be found useful for reference.

I. Table showing (approximately) the amount of gold in the world at different periods:—

Date.	Amount.
A.D. 1,	£85,400,000
1496,	11,400,000
1600,	21,000,000
1700,	70,000,000
1800,	225,000,000
1843,	400,000,000
1853,	600,000,000
1870,	1,200,000,000

II. Table showing (approximately) the yield of the principal gold-fields during the year 1867:—

Gold Fields.	Value of Produce.	Percentage of Total.
United States—		
California and Montana,	£7,862,500	28·32
Remaining States,	4,143,750	14·92
British Columbia, Canada, and Nova Scotia,	543,900	1·96
Mexico,	212,500	0·76
South America,	488,750	1·70
Central America,	637,500	2·30
Australia	6,704,375	24·14
New Zealand,	1,275,000	4·60
Russia,	3,293,750	11·89
Europe and Africa,	482,375	1·75
Borneo and East Indies,	1,062,500	3·83
China, Japan, Central Asia, and other unenumerated sources,	1,062,500	3·83
Total,	27,769,400	100·00

III. Amount of gold, silver, and bronze monies coined at the Royal Mint, London, from 1861 to 1875:—

Year.	Gold.	Silver.	Bronze.	Total.
	£	£	£	£
1861	8,190,170	209,484	273,578	8,673,232
1862	7,836,413	148,518	352,800	8,337,731
1863	6,607,456	161,172	151,648	6,920,276
1864	9,535,597	535,194	18,069	10,090,860
1865	2,367,614	501,732	57,493	2,926,839
1866	5,076,676	493,416	50,624	5,620,716
1867	496,397	193,842	33,301	723,540
1868	1,653,384	301,356	16,328	1,971,068
1869	7,372,204	76,428	20,832	7,429,464
1870	2,313,384	336,798	32,704	2,682,886
1871	9,919,656	701,514	7,616	10,628,786
1872	15,261,441	1,243,836	47,413	16,552,690
1873	3,384,568	1,081,674	46,218	4,512,460
1874	1,461,565	890,604	65,632	2,417,801
1875	243,264	594,000	69,813	907,077

IV. Fineness of the gold coins at different periods, together with the value of the troy pound, and relative value of gold and silver:—

Year.	Fineness of Gold Coins.		Pound Troy of this Gold Coined into	Comparative Value of Fine Gold and Silver.
1104	Fine Gold.		—	1 to 9·000
1227	"		—	1 to 9·000
1230	"		—	1 to 10·000
1257	"		£10 13 4	1 to 9·300
1278	"		—	1 to 10·000
	Carats	Grains.		
1344	23	3½	14 0 10	1 to 12·584
1356	23	3½	16 0 0	1 to 11·158
1464	23	3½	22 4 6	1 to 10·331
1470	23	3½	24 0 0	1 to 11·158
1527	22	0	24 15 0	1 to 11·268
1543	23	0	28 16 0	1 to 10·434
1545	22	0	30 0 0	1 to 6·818
1546	20	0	30 0 0	1 to 5·000
1549	22	0	34 0 0	1 to 5·151
1551	23	3½	34 0 0	1 to 11·000
1560	22	0	36 0 0	1 to 11·100
1604	"		33 10 0	1 to 12·109
1626	"		41 0 0	1 to 13·346
1666	"		44 10 0	1 to 14·485
1717	"		46 14 6	1 to 15·209
1816	"		"	1 to 14·287
1821	"		"	1 to 14·287
1848	"		"	1 to 15·810
1853	"		"	1 to 15·200
1873	"		"	1 to 15·500

Thus it will be seen that standard gold has continued at the same price since 1717, namely, £3 17*s.* 10½*d.* per oz. HUNT states that, for the use of the arts, not less than 1000 ozs. of fine gold are used in Birmingham alone every week, and that in the United Kingdom the weekly consumption of leaf-gold is as follows:—

	Ozs. Weekly.
London,	400
Edinburgh,	35
Birmingham,	70
Manchester,	40
Dublin,	12
Liverpool,	15
Leeds,	6
Glasgow,	6
Total,	584

Of this amount he states, on the authority of an eminent gold-refiner, that not one-tenth part can be recovered; and he adds, that for gilding metals by the electrotype, and the water or wash-gilding processes, not less than 10,000 ozs. of gold are required annually. One establishment in the Potteries employs £3500 worth of gold per annum, and nearly £2000 worth is used by another. The consumption of gold in the Staffordshire Potteries for gilding porcelain and making crimson and rose colour varies from 7000 to 10,000 ozs. per annum.

GUMS.—See VARNISH.

GUM-RESINS.—See VARNISH.

GUN-COTTON.—*Pyroxylin*, *Tri-nitro-cellulose*; *Coton fulminant*, *Coton poudre*, *Fulmi-coton*, French; *Schiess baumwolle*, *Explodirende Baumwolle*, German.—Gun-cotton is an explosive substance, produced from cotton by the action of nitric acid, or a mixture of nitric and sulphuric acids, or a mixture of saltpetre and oil of vitriol.

History.—Towards the close of the year 1845, SCHÖNBEIN announced the discovery of an explosive cotton wool, which might be used as a substitute for gunpowder. It appears from his own statement that his discovery of ozone, which he took to be a peroxide of hydrogen, led him to entertain rather peculiar views as to the constitution of acids. These views culminated in the opinion that a mixture of sulphuric and nitric acids would be found to have strong oxidizing power. Further, he believed this mixture to contain a radical very much like ozone, and hoped to effect a combination between it and certain organic bodies. Working with these notions in his mind, he soon discovered several compounds, the properties of which were so remarkable that early in 1846 he sent specimens of them to some of his English friends. From the first he was struck with the explosive power of gun-cotton, and applied himself at once to use it in guns; but although he published his discovery, he kept the method of preparation a secret until he had taken out a patent.

Soon afterwards, however, it was announced by OTTO of Brunswick, and BÖTTGER of Frankfort, that they had produced gun-cotton by treating cotton wool with strong nitric acid; and a little later KNOP showed that it was preferable to use a mixture of nitric and sulphuric acids.

Meanwhile the French chemist PÉLOUZE pointed out that in 1838 he had drawn attention to a substance of an explosive nature, prepared by the action of strong nitric acid on paper, and suggested that it might be used as a substitute for gunpowder. He had assumed that this substance was identical with BRACONNOT'S xyloidin, $C_6H_9(NO_2)O_5$, first prepared in 1813 by the action of nitric acid on starch, linen, and saw-dust; but in November, 1846, he published experiments, which proved that there were considerable differences between the two bodies, his own appearing to be identical with gun-cotton.

Such is a brief history of the discovery of this substance. It would appear that little attention was paid to the work of the French chemists, until SCHÖNBEIN showed that gun-cotton—and he was undoubtedly the first to do this—was superior to gunpowder in explosive energy.

The new compound attracted the attention of many chemists, who investigated its properties and chemical composition; but, as will be seen from the following table, the formulæ given for the latter varied very much:—

Pélouze (1846),	$C_{12}H_{11}N_2O_{21}$	$= C_{12}H_9O_9,2(HO,NO_5)$
Péligot,	$C_{12}H_9N_3O_{24}$	$= C_{12}H_9O_9,3NO_5$.
Von Kirchhoff & Reuter,	$C_{12}H_9NO_{14}$	$= C_{12}H_9O_9,NO_5$.
Fehling,	$C_{12}H_{10}N_2O_{20}$	$= C_{12}H_{10}O_{10},2NO_5$.
Porret & Teschemacher,	$C_{24}H_{16}N_8O_{56}$	$= 2(C_{12}H_8O_8,4NO_5)$.
Pélouze (1847),	$C_{24}H_{17}N_5O_{42}$	$= C_{24}H_{17}O_{17},5NO_5$.
Schmidt and Hecker,	$C_{12}H_5N_5O_{30}$	$= C_{12}H_5O_5,5NO_5$.
Gladstone,	$C_{24}H_{15}N_5O_{40}$	$= C_{24}H_{15}O_{20},5NO_4$.
W. Crum,	$C_{12}H_7N_3O_{22}$	$= \begin{cases} C_{12}H_7O_7,3NO_5. \\ C_{12}H_7O_{10},3NO_4. \end{cases}$

The symbols represent the old atomic weights. The formulæ are derived from different data—some from analyses, and others from the increase of weight which cotton undergoes when transformed into pyroxylin.

Thus, the formula given by Pélouze in 1846 was founded upon the tolerably constant increase in weight (between 68 and 70 per cent.) which cellulose underwent when acted on by strong nitric acid, or a mixture of nitric and sulphuric acids. But in 1847 he fixed the increase of weight at between 74 and 76 per cent., and this, together with the results of direct analyses, caused him to give the second formula.

These differences would appear to show that he was working at different times with different products; and the statements made by other experimenters with regard to the increase of weight clearly indicates the varied nature of the substances they obtained. Von Kirchhoff and Reuter found an increase of weight of 76 per cent., Porret and Teschemacher only 54 per cent., while Teschemacher afterwards found the increase to be 69, and W. Crum 78 per cent. The last-named chemist suggested the formula now given for tri-nitro-cellulose, but the discrepancies observed between the results of different experimenters remained unexplained.

In 1847 J. H. Gladstone published a paper, in which he attempted to show the cause of these discrepancies, and in which the behaviour of gun-cotton with various solvents was described. He found the increase of weight to vary from 73·7 to 75·2 per cent.; but by altering the proportions of the acids, and the ratio between the weights of these and the cotton employed, he obtained products showing an increase of weight from 51·74 to 73·1 per cent. The latter was obtained by using a large quantity of the mixed acids (2 measures of strong sulphuric acid to 1 of nitric, specific gravity 1·502), the former by using just sufficient acid to wet the cotton thoroughly. Moreover, by neutralizing the excess of acid with ammonia, in the experiment which gave an increase of only 51·74 per cent., and evaporating to dryness, he was able to show that it contained much organic matter, in other words, that a part of the cellulose had been converted into a substance soluble in the acids employed. As the xyloidin discovered by Braconnot is soluble in nitric acid, being precipitated on dilution with water, Gladstone was led to examine whether any alteration could be effected upon gun-cotton by similar means. He found that an acid of specific gravity 1·45 dissolved pyroxylin, and gave on dilution a precipitate which weighed only four-fifths of the original gun-cotton. This new product dissolved in strong sulphuric acid in the cold, and was charred by that acid at a temperature below 180° Fahr. The same substance was obtained from pure cotton by the action of nitric acid of the same strength, specific gravity 1·45. The analyses of this substance, and the increase of weight sustained by cotton when transformed into it, as well as the decrease of weight which gun-cotton suffered when likewise transformed, led Gladstone to the formula, $C_{12}H_{17}(NO_2)_3O_{10}$ (old notation), as expressing its composition. To distinguish it from gun-cotton, he proposed to give it the name cotton-xyloidin.

In 1854 Hadow published a series of experiments, showing that when cotton was acted on by mixed nitric and sulphuric acids, a number of different substitution products were obtained. These may be regarded as cellulose, $C_6H_{10}O_5$, in which peroxide of nitrogen from the nitric acid replaces different quantities of hydrogen, the action depending on the strength of the acid used. According to Hadow, there are three principal products:—(1.) $C_{18}H_{21}(NO_2)_9O_{15}$, insoluble in a mixture of ether and alcohol, but soluble in acetic ether, prepared with a mixture of 2 atoms of nitric acid, HNO_3, 2 atoms oil of vitriol, H_2SO_4, and 3 atoms water; (2.) $C_{18}H_{22}(NO_2)_8O_{15}$, soluble in ether-alcohol, and insoluble in glacial acetic acid, produced when the mixture contains half an atom more water than in (1.); (3.) $C_{18}H_{23}(NO_2)_7O_{15}$, soluble in all these liquids, produced when the acid mixture contains 1 atom more water than in (1.).

The name pyroxylin has been given to these various bodies. The most highly nitrated product, $C_{18}H_{21}(NO_2)_9O_{15}$, which is now written $C_6H_7(NO_2)_3O_5$, is called tri-nitro-cellulose or tri-nitric-cellulose.

Since the publication of these results by Hadow, another formula has been given for the most highly nitrated body by Pélouze and Maury; but in 1866 Professor Abel published an extensive series of analyses which very strongly confirmed the truth of Hadow's results.

The formula now given for tri-nitro-cellulose, $C_6H_7(NO_2)_3O_5$, implies what we have already stated, that it is cellulose in which three atoms of hydrogen have been replaced by three molecules of nitric peroxide. That it contains nitric peroxide is shown by the action of caustic potash and one or two reducing agents, such as sulphate of iron, or an alcoholic solution of potassic sulphydrate. The first dissolves the gun-cotton, and gives a solution containing amongst other things nitrate and nitrite of potash, just the substances formed by the action of potash on nitric peroxide. Sulphate of iron and sulphydrate of potash transform the gun-cotton back to cellulose, the latter reagent also yielding nitrate of potash and a little ammonia.

As tri-nitro-cellulose is the only product adapted for use in gunnery, it is best to reserve the name

gun-cotton for it. The lower compounds, which are soluble in alcohol and ether, are used for the preparation of collodion.

Manufacture.—Immediately after the discovery of gun-cotton, many experiments were performed with a view to its application as an explosive agent, and its manufacture commenced on a large scale; but several serious and unexplained accidents occurred. HALL BROS., of Faversham, who added the manufacture of gun-cotton to their gunpowder works, had an explosion as early as 1847, which blew up the factory, killing every man at work in the place. The gun-cotton which was left was buried in the earth by the desire of the proprietors. On the 17th July in the next year 1600 kilos. of gun-cotton exploded at Bouchet, near Paris. This explosion was so violent that walls from 18 inches to a yard in thickness were reduced to powder, and heavy weights hurled to great distances. These and other accidents, together with the decisions of committees appointed by the French and German governments, appeared to destroy the hopes with which the manufacture had been commenced. The French Commission, after experimenting six years, reported that, "In the present condition of things there is no use in continuing the experiments in relation to the employment of gun-cotton in warlike arms."

But the difficulties which thus appeared to rise were partially overcome by the patience and perseverance of an Austrian artillery officer, General VON LENK, who discovered the cause of previous failures, made the process of manufacture one of safety and profit, and began, under the auspices of the Austrian government, an extensive series of experiments on the best methods of applying it to gunnery.

The development of the manufacture in Austria naturally attracted the attention of the European governments, and Major YOUNG was sent from England to learn all that the Austrians would communicate. In 1862 a committee was appointed by the British Association to inquire into the application of the new explosive to warlike purposes. This committee consisted of three chemists, Dr. GLADSTONE, Professors W. A. MILLER and FRANKLAND, and six mechanicians, WILLIAM FAIRBAIRN, J. WHITWORTH, JAMES NASMYTH, J. SCOTT RUSSELL, J. ANDERSON, and Sir W. G. ARMSTRONG. In the following year, at the Newcastle meeting, they presented a report, from which we take some of the information contained in this article. The committee had the advantage of General VON LENK'S attendance and service, he having been allowed to come and give evidence by the emperor of Austria.

In the manufacture of gun-cotton the object is to produce the most highly nitrated product, and General VON LENK found that, in order to insure the production of this compound, it was necessary to adopt several precautions, the most important of which are thus specified.

1. The cleansing and perfect desiccation of the cotton previously to its immersion in the mixed acids.

2. The employment of the strongest acids procurable in commerce.

3. The steeping of the cotton in a fresh strong mixture of acids after the first immersion and partial conversion into gun-cotton.

4. The continuance of the steeping for forty-eight hours.

5. The thorough purification of the gun-cotton thus produced from every trace of free acid, by washing the product in a stream of water for several weeks; subsequently a weak solution of potash may be used, but this is not essential.

Full details of all the processes necessary were given by General VON LENK. He also supplied the committee with much information as to the properties, powers, and modes of using gun-cotton. One of the features of his system as carried out at Hirtenberg, was the washing of the purified gun-cotton in a solution of soluble glass (silicate of soda). The object of this appears to have been twofold. The stability of the gun-cotton was decreased by the presence of free acids, and the soluble glass would neutralize any traces of these, which had not been washed away. Moreover, during a subsequent exposure to the air, the remaining silicate was decomposed by the carbonic acid of the air, with the formation of carbonate of soda. The latter was washed out by water, and the insoluble silica deposited in the fibres was said to be useful in effecting a retardation of the combustion of the gun-cotton. Professor ABEL, however, came to the conclusion that this process did not exert any practical influence upon the properties of the material, the only result being the addition to the mineral constituents of a small proportion of silicate of lime. In this conclusion he agreed with three German chemists, Professors REDTENBACHER, SCHRÖTTER, and SCHNEIDER, who were appointed to report on VON LENK'S gun-cotton to a German committee of inquiry, of which Major VON FICHTENSTAMM was president.

That VON LENK'S process really gave tri-nitro-cellulose may be seen from the following analyses, taken from the report of the above-mentioned German chemists:—

In 100 parts.	Calculated.	Found.		
Carbon, ...	24·3	24·4	23·9	25·1
Hydrogen, ...	2·3	2·7	2·4	3·0

We shall not enter more fully into the details given by General VON LENK, as his method has been somewhat modified. It will be seen from the following description of the process as now carried on, how far the various points in his statement are now attended to.

It should be stated that F. A. ABEL, by the permission of the Secretary of State for War, joined the British Association committee, and placed at its disposal all the information acquired by our government from the Austrians, and from ABEL'S own researches. Not long after, our government appointed a committee, with General SABINE as president, to make experimental inquiries, and a government factory was commenced at Waltham Abbey. In the article on EXPLOSIVE'S a short account

is given of the manufacture of gun-cotton as it was conducted at the government establishment, but the following is a detailed description of the process and machinery adopted by Messrs. PRENTICE & Co., of Stowmarket. The references are to the two Plates headed "Explosives," which will be found at the beginning of this volume.

Clean cotton waste, picked as free as possible from foreign matter, is brought into a uniform and open condition by being passed through a carding engine shown in Plate I. The rolls thus obtained are dried in a triple cylinder, called a drying tube. The cotton is placed in the central chamber, while steam circulating in the surrounding one keeps the whole tube at a high temperature. By means of a blower attached to the pipe a blast of air enters the outside chamber at the bottom, and heated as it is during its passage to the top, is led to the central tube and forced through the loose mass of the cotton. The latter is in this way rapidly robbed of its moisture, and when completely dried is placed in large tins and carefully covered. After standing in these till quite cold, the cotton is weighed out in quantities of 1 lb. each, and carried by a boy to the dipping vessel, Plate I. Here each pan is charged with about 12 gallons of a mixture of 3 volumes of sulphuric acid, specific gravity 1·84, and 1 volume of the strongest nitric acid, the whole being kept cool during the action by currents of cold water, which circulate round the vessel. In this mixture the cotton is dipped, and after it has been in about three minutes, the workman lifts it on to a grating just above the acids. Then, with a movable lever, he gently squeezes it until, roughly speaking, it retains about ten times its weight of the liquid. Thus saturated with the acids, it is allowed to remain in well-covered earthenware pots, Plate I., for twenty-four hours; the pots during this time standing in a shallow trough containing water, to keep down the temperature. The chemical change in the cotton is now complete, and the further processes are for washing and pressing. First the large excess of acid is driven off by a centrifugal machine, a circular vessel into which the contents of the several pots can be emptied at once. When charged, the central part (see Plate I.), whose side is perforated by a great number of holes, is made to revolve at such a rapid rate that the liquid acid is nearly all thrown out. This waste acid is caught by a jacket surrounding the revolving portion of the machine, and collected in a receiver. On leaving the centrifugal machine the gun-cotton has to be washed. This operation requires great care, because the acids which the gun-cotton yet retains would give rise to a considerable development of heat if mixed slowly with water. At such an increased temperature the gun-cotton would be decomposed, or "fired" as it is technically called. At Stowmarket an artificial cascade is made by leading a stream of water along a trough and allowing it to fall from a height into the washing vessel, Plate I. The gun-cotton is thrown on the falling stream and is immediately carried deep down into the vessel, the agitation of the water being further promoted by the workman. In this way the cotton comes in contact with such a large quantity of water that the rise of temperature is inappreciable, and the pyroxylin becomes almost altogether free from acids. But to perfect the washing, the cotton is subjected to the action of water in storing tanks for one, two, or three weeks, and afterwards boiled in large vats by the injection of steam. By this latter operation the less stable compounds are destroyed and extracted, and the purified gun-cotton is transferred to the beating tank, Plate I. This is a simple contrivance for converting the cotton into pulp. It consists of a drum with a large number of closely set ridges or teeth on its circumference, while underneath is a fixed ridge which nearly touches the teeth of the drum as the latter revolves. Hence, when the machine is working, the gun-cotton is drawn between these ridges and beaten till it forms an emulsion of very thin consistency.

The pulp is now removed from the tank to a "poacher" (Plate II.), where it is agitated with a larger quantity of water by a wheel. A strainer at the bottom of the poacher enables the workman to draw off the water and replace it by a fresh supply, in which the gun-cotton is washed until it answers the heat test, which the chemist now applies. When his report is favourable, the pulp is transferred to the vat (Plate II.), and mixed with a small quantity of caustic soda. The further processes of abstracting the water and moulding the pulp into given weights and shapes are performed in hydraulic presses of various kinds, two of which are shown on Plate II. In the figure on Plate II. is shown the cylinder of the press and also the ram. Other cylinders are movable round a vertical support, and have a closely perforated plate fixed on their bottom ends. The cylinder being brought into the proper position, a measured quantity of the pulp is poured down a pipe. By the action of a suction pump connected with a tap, most of the water is at once drawn off through the perforated bottom of the cylinder. The latter is then turned round to the position, and the press set to work. In a very short time the gun-cotton is taken out in the form of a slab or cylinder. These are further pressed in a more powerful machine, also shown in Plate II., and afterwards soaked in water till they contain about 25 per cent. of that liquid.

Under the specification of Professor ABEL, the gun-cotton is sometimes granulated by the following process. When the gun-cotton in the poacher has been washed sufficiently to pass the chemical tests for purity, it is placed in a centrifugal machine similar to that used for the purpose of extracting the large excess of acids after the conversion into gun-cotton (see Plate I.). In this machine the pulp loses water till it contains only about 33 per. cent., and is reduced to a condition more or less fibrous. It is then taken to the granulating room, where it is first passed through sieves or perforations, which break up the mass, and to some extent determine

the ultimate size of the granules. The material is then transferred to a revolving drum, like a large barrel mounted on a horizontal axis, in which it is kept revolving for about a quarter of an hour. Water is from time to time sprinkled on the granules, or the sides of the drum are moistened, to assist the hardening action. The drum, in revolving, carries the granules partially round with it, but under the action of gravity they descend after reaching a certain point, and thus are caused to roll over one another. The speed of the drum decides to a great extent the rapidity of the granulating process. The speed should be just such that the material is carried by the drum sufficiently forward on the surface to be compelled to run down sharply. On the other hand, it must not be too great, as none of the granules must be carried round by the centrifugal force of the drum. On removal from this machine, the completing operation is the removal of the water, either to dryness or to the extent desired. For mining purposes, the gun-cotton is packed in water-proof cartridges in a state containing 25 per cent. of water. These are issued to the mines, and are used in that state, the firing of the wet material being easily accomplished by means of a three-quarter ounce priming charge of dry gun-cotton, fired by a cap, as explained afterwards.

The great difference between the process of manufacture described above, and that of VON LENK, consists in the introduction of the pulping operation devised by ABEL. Two important ends were attained by its agency. Firstly, it admits of very searching processes of purification; and secondly, it admits of reliable testing. Before its introduction the testing of gun-cotton could not be reliably performed on some tons of material existing in the form of yarn or cotton waste, but of which no intimate mixture could be made. When the same material is beaten into pulp and some thousand pounds weight stirred in a vat with a large quantity of water, it is evident that a sample drawn from the vat represents the whole. The pulping process therefore not only secured the more thorough washing of the gun-cotton, but introduced the valuable security in sampling for test, which had previously been wanting.

The compressed gun-cotton is finally packed in wooden cases, lined with gutta-percha and pitch.

From the conditions of the manufacture it will be seen that water has no injurious effect upon it.

In practice it is found that 100 parts of cleansed and dry cotton fibre furnish about 175 parts of pure dry gun-cotton, the theoretical quantity obtainable being 183 parts.

Properties of Tri-nitro-cellulose.—Before it has been reduced to pulp, gun-cotton has the same appearance as the original fibre, but it is harder to the touch. It is neutral to test paper, and has neither taste nor smell. It may be distinguished from ordinary cotton under the microscope, as it does not depolarize light. It is insoluble in water, alcohol, ether, and glacial acetic acid. Dilute acids and alkalies have no action upon it; but a lower substitution product is formed by the action of nitric acid of specific gravity 1·45, which product weighs only four-fifths of the original gun-cotton. Strong sulphuric acid dissolves it with difficulty; and if the solution be heated to a high temperature, it gives off carbonic acid and nitric oxide without turning black. Caustic potash also dissolves gun-cotton, the solution containing nitrate and nitrite of potassium. Sulphate of iron and an alcoholic solution of sulphydrate of potassium convert the pyroxylin into ordinary cotton, with the production of nitrate of potassium and a little ammonia when the latter reagent is used.

Dry gun-cotton will absorb about 2 per cent. of moisture from the air. When it contains more than this quantity of water, it will on being exposed for a sufficient length of time give off moisture till the same percentage is reached.

Much uncertainty prevailed for a long time as to whether gun-cotton was liable to spontaneous combustion or not. On the one hand, it was known to have been stored in Austria for twelve years with no trace of decomposition. During the war in Italy in 1859 some of the gun-cotton taken there was thrown aside, and exposed in black boxes to the hot sun for many years, yet it was found unaltered. On the other hand, it was admitted by the three German chemists already named, Professors REDTENBACHER, SCHRÖTTER, and SCHNEIDER, that some varieties of gun-cotton, inclosed in a glass tube with a piece of litmus paper, often manifested an acid reaction at ordinary temperatures. But Professor ABEL, in the course of a long and valuable series of researches, showed that decomposition was due to impurity, generally resulting in the process of manufacture, from the action of the acids on resinous matter in the imperfectly washed cotton, and demonstrated the fact that gun-cotton is a very stable body.

According to BARON VON EBNER, tri-nitro-cellulose will not explode below a temperature of 136° C. (277° Fahr.); but several other experimenters have found that the exploding point is higher than this, especially if the cotton has been washed in soda. MELSENS gives 180° C.

The products of the explosion differ very much according to circumstances. For instance, Lieutenant VON KAROLYI found the following to be the percentage composition of the resulting gases:—

	By Volume.		By Weight.
Carbonic oxide,	28·55	....	28·92
Carbonic acid	19·11	....	30·43
Marsh gas	11·17	....	6·47
Nitric oxide,	8·83	....	9·59
Nitrogen	8·56	....	8·71
Aqueous vapour,	21·93	....	14·28
	98·15	....	98·40

These gases were the result of an experiment performed in the Torricellian vacuum of a glass tube. The cotton was fired by sending a current of electricity through a platinum wire fused in the glass, till the metal became sufficiently hot. In a repetition of the experiment with a larger quantity of cotton—that is, when the pressure caused by the

explosion would be greater—it was found that the proportion of the nitric oxide diminished, while the nitrogen increased. As this appeared to show that the deoxidation of the nitrogen was brought about by greater pressure, Lieutenant VON KAROLYI performed the explosion in a vessel, which was so arranged as to give way just when the full power of the gases produced was felt, this vessel being placed in an iron globe exhausted of air. The following table shows the composition of the gases obtained in this way :—

	By Volume.		By Weight.
Carbonic oxide,	28·95	....	29 97
Carbonic acid,	20·82	....	33·86
Marsh gas,	7·24	....	4·28
Hydrogen,	3·16	....	0·24
Nitrogen,	12·67	....	13·16
Aqueous vapour,	25·34	....	16·87
	98·18	....	98·38

The difference between these numbers and 100 VON KAROLYI reckoned as separated carbon. 100 grains of the gun-cotton yielded about 325 cubic inches of gaseous matter at ordinary temperature, supposing the various products to remain in the condition of gas. It will be observed that the products of explosion contain no solid substances.

By varying the conditions of pressure, confinement, &c., under which the combustion took place, ABEL succeeded in obtaining a still greater diversity in his results. In these experiments the resulting gases were more complex in character than those obtained by VON KAROLYI, and generally contained nitrous acid, nitric oxide, and cyanogen. As one result of his work, ABEL produced fuses and slow matches of gun-cotton, in which the time occupied in burning could be accurately regulated.

Having thus stated the principal properties of gun-cotton, we proceed to give some information as to its applications.

From the time of its discovery by SCHÖNBEIN, attempts have been made to use gun-cotton in artillery, but with varying success. When a loose mass of gun-cotton is ignited in the air it burns rapidly away without any explosive effect; but if the ignition take place in a closed chamber, the gases first produced immediately penetrate the mass of the cotton, and the whole is instantaneously decomposed. Now, the object of the artillerist is to produce a force that shall first start the ball, and then gradually increase its speed, until it is discharged with the required velocity. But the explosion of gun-cotton in a gun under ordinary circumstances is so rapid that the weapon feels the full strain before the ball moves, and thus the chance of bursting is much increased.

Many suggestions have been made to overcome this difficulty. Baron VON LENK thought he had done so, and declared that it was only necessary to give the gun-cotton room enough in order to obtain a slower explosion. For small arms he used thread or spun yarn gun-cotton, woven into a web, and enclosed the web in stiff cylinders of pasteboard. For larger guns the yarn was wound round a bobbin, a hollow tube of paper or wood. The object of this is to insure in all cases the length of chamber necessary in the gun for the most effective explosion. In some cases different layers of the explosive were separated by layers of paper. Baron VON LENK was able to claim certain advantages for his gun-cotton prepared in this way. There was no residue, no smoke, and the gun was not heated so much. It was shown experimentally that 100 rounds were fired with a six-pounder in thirty-four minutes, the gun being raised in temperature by gun-cotton to only 122° Fahr., whilst 100 rounds of gun-powder took one hundred minutes, and raised the temperature to such a degree that water was instantly evaporated from the surface of the gun. 180 rounds were fired with gun-cotton before it was thought dangerous to proceed with the experiment. But experience has not fulfilled the expectation of VON LENK, and since the vast improvement in the manufacture caused by the introduction of pulping, the efforts to produce an explosive which can be used in guns have taken other directions. These, and the present relation of gun-cotton to fire-arms, are summarized in the article on EXPLOSIVES.

For other military and mining purposes, however, gun-cotton is very efficacious. Until 1872 it was thought necessary to confine gun-cotton in some strong vessel before its full power could be developed; but in that year Mr. E. O. BROWN, of Woolwich, showed that it was possible to produce the most violent explosions with gun-cotton while in an unconfined and even wet condition. This discovery consists in starting an initial detonation, and the method now adopted is the following:—The wet gun-cotton is placed in the position required, and a small cylindrical charge of dry compressed gun-cotton is laid in contact with it. This charge, called a "primer," is provided with a hole drilled on the axis of the cylinder, into which a detonator is fixed. A detonator is simply a percussion cap, such as is used with fire-arms, made a little more powerful. It is one quarter of an inch in diameter by one and an eighth inch in total length, and it contains five times the weight of fulminating powder common to ordinary percussion caps. Rather less than one-half of the total length of the copper tube is occupied by the fulminate, the remainder being reserved for a fuse. The fuse, generally prepared from specially made gunpowder, having been ignited, brings about the detonation of the fulminate; and the violent decomposition of the latter suffices, by the help of the primer, to explode the mass of wet gun-cotton. In this way explosions of very great violence are produced.

The value of the above discovery lies in this—that the wet gun-cotton is an absolutely uninflammable substance, and will not burn at all till it has been exposed to a high temperature for a considerable time. Hence, there is little or no fear of accident under any ordinary circumstances, and yet it is quite easy to bring about explosion by the simple means described.

Referring to the uninflammability of this wet gun-

cotton, and immunity from explosion when merely lighted or ignited, the committee appointed by Mr. Cardwell in 1871 for the purpose of considering and reporting upon the general question of the manufacture, storage, and use of gun-cotton, affirmed that their experiments "conclusively proved that gun-cotton, in the ordinary damp state in which it is stored, and to the extent of 1 ton, will even under the most trying conditions of confinement burn away without explosion when once ignition has been established."

The force developed by the explosion of gun-cotton is much greater than that obtained from an equal weight of gunpowder. If they be compared when acting in a closed chamber, the eruptive power of the cotton will be found to be nearly five times that of the powder. In an unconfined space the difference becomes still greater; the incisive effect obtained by the detonation of gun-cotton, as described, being more than ten times that of an equal weight of gunpowder. It is therefore evident that much saving will accrue to the miner by the use of the former instead of the latter. His shot holes may be drilled of only one-half the usual diameter, and yet be able to do the same work.

When duly rammed home, granulated gun-cotton assumes a density equal to about 50 lbs. per cubic foot, or 0·463 oz. per cubic inch. The approximate weight of wet granulated gun-cotton that a shot hole of a given diameter and depth will contain, when properly charged, may be calculated from the following formulæ:—

$$\cdot00035\ D^2 \times L = W.\ lb.$$
$$\cdot0056\ \ D^2 \times L = W.\ oz.,$$

in which D = diameter of hole in terms of eighths of inches; L = length or depth of explosive (when rammed) in terms of inches; W. lb. = weight of granulated wet explosive in pounds; W. oz. = weight of granulated wet explosive in ounces.

For dry gun-cotton the constants are respectively:—

·00028 for the weight in pounds,
·00448 for the weight in ounces,

and for gunpowder weighing 62 lbs. per cubic foot, or 0·574 ozs. per cubic inch—

·0004375 for the weight in pounds,
·007 for the weight in ounces.

Thus a shot chamber $1\frac{1}{4}$ inch, or ten-eighths of an inch in diameter, by 5·9375, or $5\frac{15}{16}$ inches in depth, will contain of wet granulated gun-cotton ($10^2 \times 5{\cdot}9375 \times {\cdot}0056 = 3{\cdot}325$) say $3\frac{1}{3}$ ozs.

It will have been noticed that there is a considerable percentage of carbonic oxide in the gases produced by the explosion of gun-cotton. The well known poisonous nature of this gas being considered, it is easy to see that in driving headings in tunnels and mines, and in sinking shafts, a certain amount of time must be lost after each explosion in waiting for this gas to diffuse itself. In order to do away with this inconvenience, nitrated gun-cotton is sometimes used. This is produced by incorporating ordinary pulp with saltpetre or nitrate of soda in the proportion of 40 parts by weight of one of these salts to each quantity of pulp capable of producing 100 parts of gun-cotton, weighed in the dry state. When these nitrated compounds are exploded, the products of combustion furnish but little, if any, carbonic oxide. They are harder, less liable to flake, and less inflammable, without being less efficient than ordinary gun-cotton.

It is sometimes necessary to dry small quantities of gun-cotton. This is accomplished in the open air, the apparatus consisting of a tray or drawer fitted with a false bottom, made of perforated sheet copper, upon which the charges rest during the operation of drying. Over the tray is a shallow reservoir for steam, and this again is covered by a sheet of iron in a curved form, to protect the upper surface from the cooling effects of currents of air and showers of rain. The gun-cotton is thus dried by radiant heat; and as the temperature of the steam is not allowed to rise above 215° Fahr. (a pressure of 1 lb. per square inch above that of the atmosphere), no difficulty is experienced or danger incurred in the operation.

Collodion.—It has already been stated that the product of the action of sulphuric and nitric acids on cellulose varies with the proportion of water present. We have hitherto been dealing with gun-cotton properly so called—namely, that produced by the strongest acids. The other compounds, although not adapted for use as explosives, have found several useful applications. Their value depends mainly on their solubility in a mixture of ether and alcohol; the collodion of the photographer, the most important of them, being obtained from pyroxylin by dissolving it in this menstruum. The following formulæ for the production of this soluble pyroxylin are taken from Hardwicke's "Manual of Photography:"—

(1.) Strong sulphuric acid,	6	fluid ozs.
Dried nitre,	$3\frac{1}{2}$	ozs. (avoir.).
Water,	1	fluid oz.
Best bleached and dried cotton wool,	60	grains.
(2.) Sulphuric acid, spec. grav. 1·845,	18	fluid ozs.
Nitric acid, spec. grav. 1·457,	6	"
Water,	$5\frac{1}{4}$	"
Dried cotton wool,	300	grains.

Other formulæ are given, and in all processes several precautions are necessary to insure a good yield of soluble pyroxylin.

The acids and water, or the acid, nitre, and water, are mixed first. A considerable amount of heat is developed in this process; and as it is necessary that the conversion should be conducted at a temperature near 140° Fahr., the mixture is allowed to cool down to that point before proceeding. If the temperature become lower, the vessel containing the mixture is floated on warm water till the operation is completed, in order that the acids may be at the right temperature throughout. The cotton, in tufts about the size of a walnut, is thrown into the acids, allowed to remain there a short time, and then quickly washed in a large excess of water. The pyroxylin obtained is dissolved in a mixture of ether and alcohol, the proportions of these employed depending on the

purpose for which the collodion is required. For positives, about 3 of ether to 1 of alcohol is used, 48 grains of pyroxylin being dissolved in 6 fluid ozs. of this mixture. For negatives, 2 of ether to 1 of alcohol is employed, 15 fluid ozs. of the mixture being taken to dissolve 120 grains of pyroxylin.

Besides its use in photography, soluble pyroxylin is employed for the production of an artificial skin to wounds, and for the manufacture of small balloons. For the latter purpose the etherial solution is poured into a flask, and after being made to run all round the inside, is drained off. The remaining ether is then blown out by a current of air, a thin film of pyroxylin being left in the flask. After the edge of this film has been loosed by a knife, the balloon is withdrawn by placing a tube in the neck and abstracting the air.

Soluble pyroxylin is not so stable as gun-cotton, and should not be kept in large quantities. It is best preserved in a clean, well-ventilated place.

GUNPOWDER.—*Poudre à canon*, French; *Schiesspulver*, German.—A mixture of saltpetre (potassium nitrate), sulphur, and charcoal in variable proportions.

The invention of gunpowder formed a grand epoch in the world's history. TOMLINSON ascribes it to BARTHOLD SCHWARTZ, a German monk and alchemist, and the date of the discovery is supposed to be about the year 1320. The prior claims of ROGER BACON, whatever they be, are however unquestionable, as this substance is described in his writings about the year 1270, or half a century before the supposed discovery by SCHWARTZ. But even BACON himself has as little title to the invention as his imagined rival; nor, indeed, when his own description of this then wonderful compound is examined can it be perceived that he makes any claim to be the discoverer. On the contrary, he quotes it as a well-known substance in common use all over the world for making squibs for the amusement of children—so pertinacious are vulgar errors. DUTENS attempts to show that the claim, which certainly does not belong to BACON, is removed to MAGNUS GRÆCUS, whose manuscript he quotes, and from which he presumes BACON derives his knowledge of the invention; although, by his own showing, BACON need not have consulted an obscure writing for an invention of general notoriety. In the same manuscript are contained directions for making a rocket, which are such as to prove that the nature of this firework was thoroughly understood. It is even remarkable that he recommends the charcoal of willow wood, which the moderns have found by experience to be amongst the best for such purposes.

Thus far the date of the origin of gunpowder has been traced not only beyond BACON, but beyond this supposed predecessor, as he himself professes to be a *compiler*, not an author of the "Liber Ignium," as he denominates his treatise. If, in attempting to ascend still higher, the evidence becomes more rare and illegible, there are still insuperable facts to prove that its antiquity is far greater, however impossible it may be to approximate to the date of the invention, much less to assign that which appears to be buried amongst the obscurities of oriental learning. The question of gunpowder as applied to artillery is a separate one; but there is abundant reason to believe that this compound was not only used in some form or other as an explosive and combustible substance, but that it was applied even to military purposes—it may be in the shape of rockets or other fireworks, which, for objects of amusement at least, have been familiar to the Chinese beyond all record.

The earliest date to which a knowledge of gunpowder can be referred, in defect of a sufficiently remote acquaintance with oriental history, is 355 before Christ, although, from the very nature of this attestation, it follows that it was then only known to the Eastern nations, but that it must have long been so, since even at that early period it was applied to warlike purposes. In the code of Hindoo laws, indeed, where it is mentioned, it is referred to an era which oriental antiquaries have considered as coincident with the time of MOSES. But the evidence to which more particular allusion is made is found in a passage of the "Life of Apollonius Tyanæus," by PHILOSTRATUS, the purport of which is that ALEXANDER was unwilling to attack the Oxydracæ, who lived between the Hyphasis and the Ganges, because they were under the care of the gods, and overthrew their enemies with thunder and lightning which they shot from their walls. The same account is given of the repulses experienced in this country by HERCULES and BACCHUS.

VITRUVIUS relates that ARCHIMEDES, in the defence of Syracuse (B.C. 212), devised an engine which threw stones with a great noise, a description which does not apply to any of the mechanical artillery of the ancients.

Of the earliest date at which it was known in China, their own evidence is defective; but UFFANO, an Italian author, affirms that not only gunpowder, but ordnance, was in use in that nation in the year 85, and that in his day cannon were remaining from the most ancient times in some of the maritime provinces, made both of iron and of brass.

There is after this a long blank; and the first author on the subject is an Arabic writer, in the Escurial collection, whose work, bearing date 1249—about twenty years before the date of BACON'S narrative—is translated by CASIRI. His description is such that it may apply both to rockets and to shells.

It has already been stated that gunpowder is a composition of indefinite quantities of sulphur, saltpetre, and charcoal. From time to time various experiments have been conducted with considerable care for the sake of determining the most convenient proportions of the foregoing substances; and, singularly enough, people have in almost every instance fallen back upon the recipes given by the most ancient writers upon the production of this article. The knowledge that powder owes its extraordinary effects to the sudden transformation of its solid constituents into permanent gases, the volume of which is enlarged by the temperature

resulting from the chemical action producing this change, will at once lead to the conclusion that all matters incapable of undergoing such a modification injure or depreciate, in proportion to their quantity, the quality and efficacy of the product.

Materials.—The ingredients for the manufacture of gunpowder, says Captain Smith, late assistant superintendent, are supplied to the Royal Factory at Waltham Abbey in the rough state, and are refined and prepared for use there; but in many private factories it is the custom to purchase the saltpetre and sulphur refined and ready for conversion into gunpowder, and charcoal ground or unground. A manufacturer who refines his own saltpetre and sulphur, and burns his own charcoal, has means of insuring the purity and uniformity of the ingredients which he makes use of, far superior to that of any system of testing, however careful. The additional security against accidents in the course of manufacture, gained by careful exclusion of all foreign matters from the ingredients during the process of refining, is of even greater consequence.

The *saltpetre* used at Waltham Abbey is exclusively that imported from India. Various descriptions of artificial saltpetre—that is, saltpetre made by chemical processes, generally by the action of potassium chloride on sodium nitrate—have been tried successfully; but as there is no economy in employing the latter, as the natural salt can be refined by a simple process, it has hitherto been preferred. It comes principally from Bengal and Oude. In these countries it occurs as a white incrustation on the soil, being also mixed with it to a considerable depth. The earth is scraped up and boiled with water, and the solution, after being concentrated by the heat of the sun and evaporated by artificial heat, yields impure crystals of the salt, which are packed in bags of course sacking. In this state the salt is known as "grough saltpetre."

Before the salt is fit to be used for powder making the impurities must be eliminated. The amount of impurity present is reckoned per 112 lbs., and in good samples does not amount to 5 per cent., and seldom exceeds 10. It is known as the "refraction" of the nitre, the term being derived from the old process used to ascertain it, viz., by fusing a small portion into a cake and examining the fracture; it has nothing to do with the optical properties of the salt. In the saltpetre market 5 per cent. is supposed to be the standard amount of impurity, all transactions taking place on that basis, but with the understanding that if the amount of impurity be greater, a reduction is to be made in favour of the buyer, and *vice versa*.

The following is a copy of three analyses of specimens of grough saltpetre:—

	Per Cent.	Per Cent.	Per Cent.
Moisture,	1·60	1·59	1·74
Sand,	·10	·21	·25
Sulphate of soda,	—	·78	3·21
Chloride of sodium,	1·00	·37	·85
Saltpetre,	97·30	97·05	93·95

The process now generally employed for removing these impurities is a very simple and effective one, and was first introduced and practised in France.—See Potassium.

The principal saline impurity in saltpetre is sodium chloride—common salt—which has a very injurious action on gunpowder, causing it to absorb moisture, whereby its power is soon considerably weakened. Saltpetre containing more than a $\frac{3}{10000}$th part of chlorides is rejected as unfit for use.

The *sulphur* used at Waltham Abbey is imported from Sicily. The finest quality, known as *Sicara firsts*, is alone employed. As imported the sulphur contains 3 or 4 per cent. of earthy impurities, having already undergone a rough purification by distillation before it comes into the merchant's hands. It is finally and carefully purified by a second distillation. Many private factories use the ordinary roll sulphur of commerce, which is simply sulphur melted and cast into moulds.

Sulphur exists in several distinct conditions or forms, two of which require special notice when speaking of it as an ingredient of gunpowder, viz., the soluble or electro-negative form, and the insoluble or electro-positive. Distilled sulphur consists almost entirely of the former; sublimed sulphur contains a large proportion of the latter. Distilled sulphur, as used in the manufacture of gunpowder, consists of masses of clear yellow crystals in the form of rhombic octahedra, and is readily soluble in bisulphide of carbon. Sublimed sulphur (known as *flowers of sulphur*) is a pale yellow powder, composed of minute particles, which do not present a crystalline structure, but which are merely minute granules consisting of insoluble sulphur, inclosing a small portion of the soluble variety. This latter form of sulphur is to a great extent insoluble in the bisulphide.

It is generally stated that the reason flowers of sulphur cannot be used for powder-making is because, having been deposited in a chamber containing a considerable amount of sulphurous and sulphuric acid, they are always found to present a decided acid reaction, which would be injurious on the finished powder; but Professor Bloxam points out that it is much more likely that the properties of the electro-positive or insoluble sulphur, of which they are in a great measure composed, may exercise an injurious effect on the action of gunpowder.

Charcoal.—The woods from which charcoal is now manufactured for powder-making appear to have been in use from a very early period. Their adoption was no doubt decided empirically, but it is not easy even now to determine why particular woods are better adapted for charcoal than others. It is stated that as early as 1414 King Henry V. ordered twenty pipes of willow charcoal to be prepared for employment in gunpowder-making.

The only woods now used in the Royal Gunpowder Factory are the *willow*, the *alder*, and what is popularly known as the *black dogwood*, but which is really the alder buckthorn, or berry-bearing alder (*Rhamnus frangula*). Though various other woods are used by private makers for coarse blasting powder, the three woods named are generally used both at home and abroad for the best gunpowders.

1. *Willow.*—The particular species of willow which finds most favour at Waltham Abbey is the white Dutch (*Salix alba*). This is one of the softest and lightest of English woods. It is of very rapid growth, a section of the wood showing wide and well-marked rings of annual increase. The wood is nearly white, and has a tolerably large circular white pith. The more rapidly the wood has been grown the less dense will it be, and the better for powder-making when converted into charcoal. For this reason wood grown in England is preferred to that grown abroad, the foreign wood, both alder and willow, being found to be closer in the grain.

2. *Alder.*—The common alder (*Alnus glutinosa*), though supposed to be of exactly equal merit with the willow, is considerably harder and denser in texture, and is not of such rapid growth. The colour of the wood is reddish-yellow; the pith is triangular in section, resembling in shape the section of a bayonet.

3. The *Black Dogwood* (for it has been so long known to powder makers by this name that it may be as well to adhere to it) is a handsome underwood of very slow growth, and is found in thickets in many parts of the south of England, and in Scotland. The name dogwood has been derived from its berries resembling those of some of the dogwoods proper.

Though the *Rhamnus* has been misnamed, there is no confusion about the wood itself. It is undoubtedly the *Rhamnus frangula*, which has found such favour with powder-makers both at home and abroad. Though the wood is found in many parts of Great Britain, the main source of supply is the Continent. The wood is dense and tough, the annual rings being very close together. The pith is circular and reddish in colour, occasionally bright red. This colour is preserved even after the charcoal is burned.

Small wood of about ten years' growth is in all cases preferred for powder making. Alder and willow of this age is 4 or 5 inches in diameter, dogwood about 1. Great stress is always laid on every trace of bark being removed before conversion of the wood into charcoal. The wood is cut in the spring when the sap is rising. Wood cut later in the year, or in winter, is perfectly as good; but the removal of the bark is a much more difficult matter. To separate it the wood must be boiled, or if that be impracticable, the whole of the bark must be shaved off with a knife or spokeshave.

The temperature at which the charring of the wood is conducted, and its uniformity, are of the highest importance for the chemical composition of the charcoal, and the temperature at which it will ignite is undoubtedly affected by the temperature at which it has been charred. Charcoal prepared at a low temperature is softer, more inflammable, and contains more gaseous elements than charcoal prepared at a greater heat, and the gunpowders made from these charcoals would be similarly affected. It is hopeless, therefore, to attempt to obtain uniform results in manufacturing powder unless means be taken to insure uniformity in the preparation of charcoal. At most foreign gunpowder manufactories pyrometers to ascertain the temperature of the cylinders are in use; but in England the process is intrusted to the experience and careful watching of the foreman. Charcoal, if properly made, should be jet black in colour; its fracture should show a clear, velvet-like surface, and it should be light and sonorous when dropped on a hard surface. Underburnt charcoal, that is, charcoal prepared at a very low temperature, is at once known by its reddish-brown colour, overburnt charcoal by its hardness and density. Two considerations, therefore, must not be overlooked in choosing a proper charcoal—namely, the nature of the wood, and the manner in which the carbonization of the same is conducted; and each demands the utmost circumspection in the manufacturer who is desirous of producing an article which will yield the greatest possible amount of force, and combine at the same time the quality of inflaming readily, as well as that of leaving the least quantity of residuary matter after its ignition.

Underburnt charcoal has found favour amongst private makers in this country and in France for some small-arm powders. It certainly renders the powder more inflammable, and consequently quicker; but it has the disadvantage of being more hygroscopic than denser charcoal. The powder is therefore more liable to suffer damage from damp. Some experiments made at Waltham Abbey with two field-gun powders, in all respects identical except the burning of the charcoal, showed that that made with underburnt charcoal gave 60 feet more velocity to a 12 lbs. shot than that made with the ordinary black charcoal.

The following analyses of charcoals made at the Royal Gunpowder Factory show that they do not vary much in chemical construction or physical qualities:—

	Ash.	Carbon.	Hydrogen.	Oxygen, with trace of Nitrogen.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Alder.	1·24	87·00	2·97	9·78
Willow,	2·02	85·82	2·88	9·28
Dogwood,	1·71	83·80	3·28	11·21

The charcoals from three different specimens of gunpowder (L.G., R.L.G., and Pellet) manufactured at Waltham Abbey in different years, when analyzed showed a very close agreement in composition.

	Ash.	Carbon.	Hydrogen	Oxygen, with trace of Nitrogen.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
L.G.	1·61	85·79	2·84	9·76
R.L.G.,	2·02	85·82	2·88	9·28
Pellet,	2·14	85·80	2·96	9·1

The average densities of the different charcoals are given by Captain Smith as follows:—

	Per Cent.
Alder.	1·37
Willow,	1·39
Dogwood,	1·30

Two points are observable in the charcoal of dogwood, namely, the low density and the amount of gases it

contains. It is probably due to these two circumstances that its combustion is more rapid.

The woods now used in most gunpowder factories were probably selected centuries ago from actual experiment, being found to make stronger powder than any others. Even in the time of MAGNUS GRÆCUS, as already mentioned in the preceding historical notice, the charcoal of willow-wood was preferred, and experience has fully proved that the charcoal of the soft woods always produces the best results. The hard woods are invariably rejected.

Wood which contains carbonate of potassium or other deliquescent salts is unfit for the purpose, and for obvious causes. This is the case in the oak, elm, fir, and other trees. But there is another reason for the badness of these kinds of charcoal, which is not so obvious, although it is evidently connected with their hardness. It appears to depend on the small proportion of hydrogen combined with the carbon in these charcoals, compared to that which exists in the produce of the softer woods. Even these can be reduced to the same state by subjecting them to higher temperatures. Thus the hydrogen is dissipated, the charcoal becoming so hard as to scratch steel; in which case, however obtained, it is unfit for gunpowder.

To test the quality of charcoal J. LOUIS PROUST uses the following simple means:—He makes a mixture of 12 grains of the charcoal and 62 of nitrate of potassium by careful grinding in a mortar, and then introduces it on a small tray into a copper tube $2\frac{1}{2}$ inches in length by 3 lines in diameter; he primes on the top of this with a little fowling powder, and when this is done, the lower part of the tube is fitted in a dish of cork, or other light material, which is floated on the surface of water. It is evident from these arrangements, analogous as they are to those under which the powder is inflamed, that the mixture which burns the more readily is that which is most suited to the manufacture. By experiments conducted in this way, and with all the precautions available under the circumstances, PROUST obtained the following results:—

Mixture of sixty-two grains of Saltpetre and twelve of Charcoal.	Time of the Combustion in Seconds.	Weight of Residue in Grains.
From hemp or hemp husk,	10	12
" stalks of asphodel,	10	12
" vine branches,	12	20
" pea stalks,	13	21
" pine	17	30
" bourdaine	20	24
" spindle-tree,	21	27
" hazel,	23	30
" maize canes,	25	38
" chestnut-tree,	26	36
" walnut-tree,	29	33
" maize	55	43
" coal-coke,	50	45
" sugar,	70	48

When submitted to the same operation, he found that the charcoal produced from starch, wheat, rice, gall-nuts, indigo, gluten, gelatin, albumen, blood, and skin, and, in fact, those derived from all animal matters, would not undergo combustion.

From the foregoing table it is evident that those which precede the charcoal from hazelwood rise in the scale of superior fitness, whilst those beneath the latter evidently descend, and are not well adapted for the manufacture.

Other experiments upon the same subject, founding the comparison of the different charcoals upon the volume of gas which they yielded when ignited with saltpetre, have been conducted by French and British chemists, and the results are tabulated below. In each case the proportions used by the former were 60 grains of nitrate of potassium to 12 of charcoal; but in the latter the calculations are made to correspond with the same standard:—

Charcoal.	Proportion of Gas in Cubic Inches.	Residue in Grains.
From French hemp stalks,	62	12
" asphodel,	62	20
" vine,	64	20
" pea stalks,	62	21
" spindle-tree,	66	28
" fir	66	30
" chestnut,	66	36
" hazel,	66	33
" lamp-black,	54	44
" coke,	54	45
" filbert,	72	30

Much of the interest which might otherwise be taken in the foregoing results of the French chemists is lost, on account of the subjects being not likely ever to enter practically, at least to any extent, into the manufacture under consideration. Below are given results arrived at in England, by operating upon the more frequently occurring woods:—

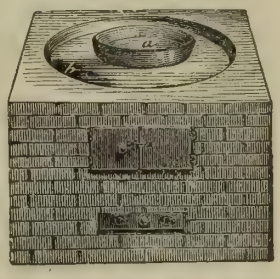
	Proportion of Gas.
Filbert,	72
Oak,	61-63
Mahogany,	58
Elm,	62
Willow—*Salix alba*,	76-78
Alder,	74-73
Dogwood—*Rhamnus frangula*,	80-82-84
Oak bark	58
Animal charcoal,	50-46-42-40
Coke,	52-48
Lamp-black,	54-52
Oak charcoal overheated	54-56
Willow charcoal overheated,	59-64-66

TOMLINSON attributes much of the difference in the latter table to the method in which the charcoal is prepared, rather than to the substance itself, since he considers that to overheat the matter in its carbonization is injurious to its power of combustion. This is evidenced by the results which the modified charcoal from oak and willow afforded; and, in fact, several researches have led to the acknowledgment of the same fact. VIOLETTE has shown that the most combustible charcoal loses this quality in proportion as the heat applied in the carbonization is raised, till ultimately, when the charring is made at the fusing point of platinum, the product obtained is so incombustible as to be ignited with difficulty even when the heat is 2282°. During his researches upon the carbonization of wood and the application of charcoal, he examined with considerable skill and acuteness the various products which most of the ordinary woods afford by charring, in reference to their combustibility in air, and the temperature of their ignition according to the heat applied in their manufacture, and also with regard to the same kind of charcoal

when subjected to an increasing heat in close vessels; the temperature at which charcoals decompose nitrate of potassium, as well when they are the result of a standard degree of heat, as when this degree has been varied in their manufacture. To these researches he has coupled the estimation of the necessary heat required for sulphur to decompose the saltpetre, and that at which it burns in air, and many others; such as the thermometric degree at which powder is ignited, the several mixtures used for the manufacture of powder with regard to the amount of their constituents, &c., to which reference will be made in their respective places. As the susceptibility of charcoal taking fire is a subject which, to those who are under the necessity of storing it for some time in magazines, is highly interesting, it may be well to lay before the reader the procedure of VIOLETTE, for the estimation of the degree of heat at which charcoals enter spontaneously into combustion.

He adopted an apparatus similar to Fig. 1, in which *a* is a small flat plate-iron basin, floating upon a bath of tin or pewter, *b*, which is heated by a fire. The pieces of charcoal, prepared in pellets 0·01 inch in length and 0·001 in thickness, were placed symmetrically in the basin, *a*, and the fire urged, thus increasing the heat of the tin bath, and consequently that of the small iron basin containing the cylinders of charcoal. The order of their inflammability was noted as each, in succession, gave indications of combustion by a luminous point appearing upon the circumference of the superior section, and which quickly enveloped the whole surface, and resulted in leaving only the ash. In the following table, the series in the column A show the order of the spontaneous ignition of the materials which had been thoroughly charred, whilst those in B represent the order with reference to brown charcoals, or such as retained a portion of their constituents, and therefore had only been but imperfectly made:—

Fig. 1.



SERIES A.				SERIES B.			
The Order of the Ignition of Charcoal.	Temperature of the Carbonization of Charcoal.			The Order of the Ignition of Charcoal.	Temperature of the Carbonization of Charcoal.		
	Fahr.		Fahr.		Fahr.		Fahr.
1			500°				
2	270°		518	"	"		"
3	280		536	"	"		"
4	290	—	554	6	250°	—	482°
7	300	—	572				
9	310	—	590	5	230	—	446
10	320	—	608	8	240	—	464
11	330	—	626	14	220	—	428
12	340	—	644	15	210	—	410
13	350	—	662	16	190	—	374
21	432	—	819	17	170	—	338
22	1023	—	1873·6	18	200	—	392
23	1300	—	2372	19	180	—	356
24	1500	—	2782	20	160	—	320

From the above, it may be inferred that charcoal, prepared at 500° Fahr., is the most liable to undergo spontaneous combustion. It is remarkable that the phenomena observed with regard to the brown or torrefied woods in the second column, was that their complete carbonization was effected (as indicated by the quantities of fumes which were disengaged from them) before they entered into ignition; *id est*, they were converted into a charcoal such as that prepared at 500° Fahr. As soon as this condition was attained, they underwent spontaneous ignition. In the second place, it is easy to see that the inflammability of the charcoals decreases in proportion as the temperature of their preparation is more elevated. To make the examination more definite than the comparative but necessarily indeterminate one above mentioned, the following process was followed:—A porcelain crucible was selected, and about 60 grammes of saltpetre fused in it. The bulb of a mercurial thermometer immersed in it showed that the melting occurred at 644° Fahr. Gradually pieces of the most inflammable charcoal, such as those prepared at 500°, were projected into the molten mass, and the crucible quickly inclosed to prevent cooling by radiation; on taking the cover off, the particles of charcoal were observed to be undergoing several commotions, but without taking fire, notwithstanding that, by increasing the heat only 1·8°, the matter burned. Hence it may be stated, that charcoal obtained at 500° ignites spontaneously at 645·8° or 646°. On increasing the temperature of the crucible and nitrate of potassium by regular increments of heat, it was found that charcoals prepared at temperatures from—

Fahr.		Fahr.		Fahr.
500°	to	536°	ignited at	680°
536	to	662	" at	698

On raising the heat a little above 698°, the charcoal resulting at 819° ignited, but the other kinds, produced at a higher heat, still remained without entering into combustion. When the thermometer ceased to indicate truly any higher heat, the bath had to be changed for one of pewter or tin. Having introduced the more incombustible charcoals, on gently raising the temperature with a charcoal fire till near the point of redness, they then began to show the first signs of combustion.

In the annexed table the results are tabulated:—

260° = 500°	....	340° — 680°
270 = 518	340 to 360	— 680 to 698
280 = 536		
290 = 554		
300 — 572	360 to 370	— 698 to 716
310 — 590		
320 — 608		
330 — 626		
340 — 644		
350 — 662		
432 — 819		
1023 — 1873·6	600 to 800	— 112 to 1472
1250 — 2282		
1300 — 2372		
1500 — 2732		
Charcoals made at temperatures which fuse platinum, ...	1250	— 2280

Violette further examined several varieties of charcoal, all of which were prepared at 572° by both the foregoing methods; they inflamed between 680° and 716°, but in no case did they take fire at a lower heat than 680°. He observed that the charcoals from light woods generally ignited a little before the product from the harder kinds, with the exception of one, which is remarkable, namely, the charred product of the fungoid excrescence of the willow tree (*agaric de saule*). The latter was observed to take fire in one instance at a temperature so low as 572°, and in every experiment at 608°. Hence it is the most inflammable of all species of charcoal; and as the above-named investigator remarks, had it been prepared at 500° instead of at 572°, doubtless its spontaneous combustion would take place at a lower temperature than even that given. It may well be inquired to what may this peculiarity be attributed; and doubtless, as Violette suggests, the organic molecular state of the substance might exercise some influence whereby its rapid ignition is induced.

To sum up these results, it will be seen—

1. That the ignition of the most inflammable of all wood charcoals (*agaric de saule*) takes place at 572°.

2. That the charcoals from different kinds of wood, when prepared at a constant heat of 572°, spontaneously ignite between 698° and 734°, according to the nature of the wood producing them; but that the product from the lighter burns quicker than that of the denser woods.

3. That charcoals from the same wood, but prepared at increasing temperatures, spontaneously undergo combustion at very unequal degrees of heat, as already shown.

After attentively considering these results, very little doubt will remain as to the best means of carbonizing the wood. To a certainty the temperature of the charcoal, as prepared by most of the methods indicated under the charring of wood, and also under Acetic Acid, exceeds the limits laid down by Violette; and therefore it follows that evidently the choice should be decided in favour of that method which furnishes the charcoal at the lowest degree of heat. There are three methods in ordinary use by which the charcoal for the powder manufacturer is prepared, namely, the pit, the furnace, and the closed retort. When pits are selected, they are made smaller than those described in the foregoing articles, and the walls and sides, together with the apertures for the introduction of air, are constructed with more care; the wood is also arranged in them with greater caution, and the combustion watched so that during the operation the whole may be completely acted upon, and no half-burned material left. In the general particulars, however, no difference exists between the methods already alluded to and this, so that it will be needless to repeat the description. The product amounts to 16 or 17 per cent. of the wood. If the carbonization is effected in furnaces, the quantity of the product will not be so large; besides the consumption of fuel will be greater than in the preceding case. In England, however, the charcoal obtained by the distillatory process in closed retorts is always preferred.

The wood is now converted into charcoal by heating it in iron cylinders, and the combustible gases pass underneath the cylinders of an adjoining set, and constitute the greatest part of the fuel. In the cylinder house of Messrs. John Hall and Sons the gases are so thoroughly economized by the method which they have originated that, whereas in 1869, 1 cwt. of coal was required for every burning, at the present time (1877) fifty burnings can be effected with 56 lbs. of coal. The amount of charcoal is generally 20 per cent. of the wood employed. After the charcoal is taken from the cylinders, it is placed in iron coolers provided with tightly-fitting lids, and allowed to stand for twenty-four hours, by which time it is quite cold, and it is then shot into store bins. A. F. Hargreaves has found by experiment that charcoal ground within two days of carbonization absorbs mechanically within its pores a large quantity of oxygen from the atmosphere; now as the condensation of all gases liberates heat, and charcoal being a bad conductor, the heat cannot escape: this becomes a source of danger. The maximum amount of oxygen (about 6·9 per cent.) is absorbed within the first two weeks, and after this no change takes place beyond those due to atmospheric agencies.

Good charcoal should submit to three tests. It ought to act as little as possible mechanically, even on copper; no salts should be extracted from it by treating it with boiling distilled water, and it ought to give out no smoke when heated. The latter test is indicative of its being thoroughly burned.

Before entering upon the description of the process for compounding the substances which constitute gunpowder, it may be well to give a few additional facts relative to the circumstances which affect the mutual decomposition of those bodies as they exist in this article, and render the phenomena of its explosion more easy of comprehension. Already some experiments of Proust have been adduced, which elicit comparative data of the explosiveness of certain varieties of charcoal when mixed intimately with saltpetre; but they do not afford any real knowledge as to the degree of heat required to bring about such a metamorphosis, although they indicate that some kinds of charcoal form more inflammable mixtures with nitrate of potassa than others. The investigation of Violette upon the temperature at

which charcoal decomposes this agent is much more definite, and consequently interesting. He found that the degree of heat which occasions the combustion of charcoal in the air is much lower than what is necessary to cause the carbonaceous matter to decompose the oxidizing agent which is incorporated with it in the powder. To determine this, he proceeded thus:—In a small porcelain crucible, heated by a lamp, which allowed the temperature to be easily regulated, potassium nitrate was melted and maintained at 680° Fahr., being the degree at which the charcoals burned in the air. Into this bath a small cylinder of charcoal appended to a platinum wire or glass rod was plunged, so that it was all submerged; although numerous bubbles of gas were disengaged, yet the carbonaceous mass did not take fire at this temperature. By raising the heat gradually to 716°, and trying the experiment at this stage, the effect was still negative, but ultimately it deflagrated after the bath had been raised to a higher degree of heat. The fusion of lead and zinc showed the thermometric effect to be above 680°; but it being incapable of melting antimony, it was evident that the heat had not reached 819°, the fusing point of the latter metal. It may be concluded therefore that all charcoals prepared between 500° and under to 819° decompose potassium nitrate at 752°, but that such as are obtained between 1832° and 2732° are not affected at the preceding nor at much higher heats, since they do not even burn upon the surface of the bath.

The same chemist determined the degree of heat at which sulphur decomposes potassium nitrate in an equally ingenious way. He found that when sulphur was thrown upon the surface of the bath of fused salt, raised to the temperature of 680° Fahr., it floated about, melted, and inflamed; the combination, however, was with the oxygen of the air, and none of the saltpetre had been acted upon. A similar result was arrived at when the bath was at 752°, or even a few degrees higher; but when it had attained 819°, the fusing point of antimony, deflagration occurred by the decomposition of the potassium salt, and the evolution of a brilliant white light and a considerable quantity of gases. In the latter experiments it was necessary that the sulphur, like the charcoal in the last-mentioned examinations, should be immersed in the fluid bath. To do this Violette had a platinum crucible about the size of a pea constructed, and to this he appended a platinum wire, which might serve as a holder to it when immersed, mouth-under, in the bath. When 0·1 grain of sulphur was melted in this tiny vessel, and plunged into the bath in the manner shown in the annexed Fig. 2, the effect was observed with considerable accuracy. Until the heat had reached the decomposing degree, the sulphur was observed to ascend in bubbles of colourless vapour through the transparent bath, and burst into a beautiful blue flame. As soon as the inflammation of the sulphur commenced within the fused saltpetre, the white light traversed the whole mass with the effect already detailed.

Fig. 2.



It was also observed that by sprinkling a little sulphur upon charcoal thrown upon the surface of the heated bath, ignition took place under the degree at which the most combustible charcoal kindles, *per se*. This occurs on account of the heat developed by the combustion of the sulphur at 480°, and which brings the charcoal to the state of redness, and consequently at which, when air is supplied, it rapidly inflames.

Proportions of the Ingredients.—The progress of improvement in determining the proportions of the constituents of gunpowder has been very gradual. In this country a long period elapsed before the present state of perfection was attained; but this cannot well be wondered at, when one takes into consideration the ignorance which existed even up to the commencement of the present century, not only with regard to the theoretical laws of science, but also in respect of the properties of bodies purely chemical.

Such compounds as saltpetre, sulphur, and charcoal in equal proportions were scarcely fit for squibs, much less for the purpose of projecting shot. Again, one finds such mixtures as saltpetre 12 parts, with 3 each of charcoal and sulphur; 27 of nitrate of potassium to 3 of each of the other ingredients; saltpetre 48, sulphur 7, and charcoal 3 parts; with many others which now-a-days appear equally ridiculous. At no very distant period, the French compositions were, saltpetre 50, sulphur 16, charcoal 34 parts; saltpetre 67, sulphur 13, charcoal 20; and again, saltpetre 84, sulphur 8, and charcoal 8 parts.

Baptista Porta was one of the first who endeavoured to ascertain the best relative quantities of the constituents, and his proportions, obtained in the year 1515, approached very nearly those now employed in France. The deductions of Guyton Morveau, Beaumé, Chaptal, Proust, and Riffault, are represented below:—

Dumas gives the proportions, saltpetre 75, sulphur 12·5, and charcoal 12·5, as the most ancient known, and states, that however these proportions have been deviated from, either from pressing circumstances of time or place, the powder manufacturer had in the end to fall back upon the above mixture as offering the best composition.

In most continental countries at the present day these proportions prevail with but little variation. In England the proportions are somewhat different, there being more charcoal and less sulphur. The proportions are saltpetre 75, sulphur 10, and charcoal 15. These proportions are rigidly adhered to in powders of all descriptions, whether for war purposes or for sporting and blasting powders. Some deviations are occasionally made, no doubt, for inferior powders where economy in manufacture is sought; and these will generally be found to consist of a diminution of the quantity of saltpetre, which is the most expensive ingredient, with a corresponding augmentation in the quantity of sulphur or charcoal. It is important, however, that powder to be

used for sporting or war purposes should have no material addition to the quantity of sulphur it contains, as an excess of this ingredient will be found to result in an attack on the metal of the piece, causing corrosion of the bore. Sulphur appears to play a very important part in the decomposition of the saltpetre, but its action has never been fully explained. It not only facilitates the decomposition by its ready inflammability, but it appears to be more accommodating in its action than charcoal. It forms two compounds, potassium sulphate and potassium sulphide, and no doubt this double action is of use in the explosion of gunpowder. With the continental proportions of ingredients little or no potassium sulphide is found in the products of decomposition; but with the English proportions it exists in considerable quantity, and it can readily be imagined that where an excess of sulphur exists, it will seek to combine with the metal of the piece from which it is fired in one or other of the two forms in which it is capable of combining. Various formulas have been attempted to account for the chemical action of gunpowder during explosion, but they are all to a great extent hypothetical, and it has been found very difficult to reconcile theory with the results obtained in practice. The affinity of charcoal for oxygen, so as to form either carbonic acid (CO_2) or carbonic oxide (CO) is the key to the process, and it has been usual to take the weight of charcoal as representing the same weight of carbon. Hydrogen being present, and taking up much oxygen from the nitrate of potassium during the explosion of the powder, accounts for this. Indeed, were it not for this excess of hydrogen which makes up for the assumed amount of carbon in the charcoal, it would be difficult to reduce the quantities of real matter in the substances within the expression of a simple formula. Analyses show that the quantity of carbon in the charcoals which are usually incorporated, varies from 68 to 90 per cent., and it is evident that when numerical quantities of the ingredients are very strictly adhered to, serious differences occur in the quality of the article, according as the charcoal is more or less rich in carbon. To adhere, therefore, to the strict proportions indicated by the numbers laid down, and which assume that the materials are pure, it becomes absolutely necessary to determine the amount of carbon in the charcoal, and regulate the quantity according to such an estimation: otherwise it is not at all surprising that two powders prepared exactly according to any given recipe, but with different materials of unknown qualities, should have very unequal effect when exploded.

The chief qualities which a good gunpowder ought to possess, are ready inflammability, complete decomposition of its constituents, the production of the largest possible volume of elastic gases, and finally, that of affording only the smallest possible amount of residue, and even that should be of such a nature as not to injure the gun.

To ascertain how far powders prepared from variable quantities of materials of the same centesimal composition differ in their balistic effect, VIOLETTE prepared a number of samples of fowling powder, each weighing about 20 kilos. (44 pounds), and submitted them to the test. The following are the results:—

No.	Percentage Composition of Materials. Saltpetre.	Sulphur.	Charcoal.	Amount of Carbon in one hundred Parts of Charcoal.	Speed of the Ball by the Balistic Pendulum.
1.	78	10	12	68	357
2.	72	9	19	68	350
3.	72	10	18	68	355
4.	71	10	19	68	361
5.	71	11	18	68	363
6.	71	9	20	68	370
7.	71	11	18	85	337

In this table No. 1 is the regular proportion, and the speed of the ball with such, supposing all the powder to be consumed, would be, according to the usual rule, 350 métres. It is surprising to observe that No. 6 in the above collection, in which the saltpetre is diminished by 8 parts, and the sulphur by 1, and the charcoal increased by 8, is a superior powder to No. 1. No. 5 also constitutes a very good powder, but its quality would be considerably deteriorated by using, instead of the charcoal containing only 68 per cent. of carbon, one yielding 85 per cent., as shown in the last. This forms a striking example of the way in which an inequality in the percentage of carbon in the powder affects it.

Inflammability of Powder.—From what has been stated in the preceding pages relative to the degrees of heat required to decompose the constituents of powder, a good inference may be drawn as to the degree of heat at which powder will take fire.

However, if a small quantity of powder be slowly heated, and the temperature be gradually raised, it will be observed that the sulphur, which is the most inflammable constituent, will begin to burn with a bluish flame at 482° Fahr., or thereabouts; and the heat developed in this partial combustion brings the other constituents into that state at which the potassium nitrate is decomposed by the charcoal, whilst the remainder of the sulphur adds to the effect by combining with the metal of the oxidizing agent, thus—

$$2KNO_3 + S + 3C = K_2S + 2N + 3CO_2.$$

The actual products are much more complicated; in place of potassium sulphide, the actual residue consists mainly of potassium sulphate; and inasmuch as this is the case whether the powder be burnt in the air or in closed vessels, or even *in vacuo*, the formation of the sulphate is independent of atmospheric oxidation.

To ascertain whether the powders, as usually manufactured, actually do ignite at the burning point of sulphur, VIOLETTE made some examinations by placing portions of the powder to be tested on the surface of a bath of tin, in which the bulb of a thermometer was immersed, the whole being heated by a small lamp: the following results were obtained—

No.	Species of Powder.	Temperature which produced Deflagration. Powder in Angular Grains.	Pulverized Powder.
1.	Blasting powder,	518°	509°
2.	War "	528·5	510·5
3.	Sporting " fine,	536	514·8
4.	do. " extra-fine,	608	518·0

Of these No. 1 was made with black charcoal, and No. 4 with brown or torrefied charcoal, the inflammability of which takes place at a much lower degree of heat than the first; still it is a matter of some surprise to find that the former, in the shape of powder, burns at a lower heat, excepting the variation in the quantity of sulphur present in them may influence the deflagration. This element is present in the four samples in the following ratio, namely, 20, 12·5, 10, and 9 per cent.; the most combustible of the powders having the largest amount of sulphur, which of all the elements is the most ready to enter into ignition. It may likewise be remarked that the size of the grain influences in some measure the temperature at which the powder burns.

Balistic or Propulsive Effect of Gunpowder.—In the explosion of gunpowder, according to Bloxam, the oxygen of the nitre converts the carbon of the charcoal chiefly into carbonic acid, part of which assumes the gaseous state, whilst the remainder combines with the potash of the nitre to form carbonate of potash. The greater part of the sulphur is converted into sulphuric acid, which forms potassium sulphate. The chief part of the nitrogen contained in the nitre is evolved in the uncombined state. The rough chemical account of the explosion of gunpowder, therefore, is that the mixture of nitre, sulphur, and charcoal is resolved into a mixture of potassium carbonate, potassium sulphate, carbonic acid, and nitrogen—the two last being gases, the elastic force of which, when expanded by the heat of the combustion, accounts for the mechanical effects of the explosion.

Some of the most recent experiments upon the explosion of gunpowder have been made under conditions very similar to those which occur in practice, the powder having been confined in a thin iron case, and suspended in the centre of a strong iron globe exhausted of air, in which the powder was fired by electricity, so that the gaseous and solid products of the explosion remained within the globe, and could be submitted to analysis. Two samples of powder were thus examined; but their composition differed from that of English powder, as will be seen by the following table:—

	I. Per Cent.	II. Per Cent.
Nitre,	73·78	77·15
Sulphur,	12·80	8 63
Charcoal, viz., carbon,	10·88	11·78
" hydrogen,	·38	·42
" oxygen,	1·82	1·79
" ash,	·31	·28

About 510 grains of powder were exploded in each experiment. The gases contained in 100 cubic inches were:—

	I. Per Cent.	II. Per Cent.
Nitrogen,	37·58	35·33
Carbonic acid,	42·74	48·90
Carbonic oxide,	10·19	5·18
Hydrogen,	5·93	6·90
Sulphuretted hydrogen,	·86	·67
Marsh gas,	2·70	3·02

The products of explosion furnished by 100 grains of each powder were—

	I. Per Cent.	II. Per Cent.
Potassium sulphate,	36·95	36·17
Potassium carbonate,	19 40	20 78
Potassium thiosulphate (hyposulphite),	2·85	1·77
Potassium sulphide,	·11	0 00
Ammonium sesquicarbonate,	2·68	2·66
Charcoal,	2·67	2·60
Sulphur,	4·69	1·16
Nitrogen,	9·77	10·06
Carbonic acid,	17·39	21·79
Carbonic oxide,	2·64	1·47
Hydrogen,	·11	·14
Sulphuretted hydrogen,	·27	·23
Marsh gas,	·40	·49

The simplest formula which can be constructed from the above numerical data is as follows:—

$$14KNO_3 + 4S + 12C = 4K_2SO_4 + 3K_2CO_3 + 8CO_2 + CO + 14N.$$

From this Bloxam calculates that 1 cubic inch of gunpowder will when exploded evolve 207 cubic inches of gas at 60° Fahr.; but that the temperature will be 5328° Fahr. at the moment of explosion, and the 207 cubic inches will become 2808 cubic inches by expansion at this temperature. The resulting pressure will be 2308 atmospheres, or 34,620 lbs., or 15½ tons upon the square inch.

The method of calculating the pressure of fired gunpowder from the products of explosion and the temperature has received very much attention; but the conclusions drawn by very able men have not been very consistent with each other, or with the well-known force of gunpowder.

About the middle of last century Robins found that the gaseous products would occupy 244 times the bulk of the powder at the temperature and pressure of the atmosphere; but at the temperature of the *extremest degree of red-hot iron*, his assumed temperature of exploded gunpowder, they would have expanded to 1000 volumes, and the pressure when confined to the space occupied by the powder would be 1000 atmospheres, or 6·7 tons per square inch

Gay-Lussac obtained 450 volumes of gas, and estimating the temperature at 1000° C., deduced a pressure of 2137 atmospheres (14·3 tons).

Piobert accepted Gay-Lussac's determination of the quantity of gas produced, but estimated the temperature at 2400° C., and thus deduced a pressure of between 4000 and 5000 atmospheres for the permanent gases alone. Counting the other products, which at this temperature he considered would be in a state of vapour at a high tension, he estimated the total pressure at 9600 atmospheres (64 tons). He considered that there were two distinct periods during the explosion of powder in a gun—one during which the solid products are in a state of vapour and add their tensions to those of the permanent gases, and another afterwards, when these products have condensed and the permanent gases alone act. This, he thinks, may account for the anomalies in the effects produced in the action of gunpowder.

Bunsen and Schischkoff obtained 193·1 volumes of gas, the production of which was attended by

the development of 619·5 units of heat; and from this, taken in conjunction with the known capacities of heat of the products, they concluded that the temperature of the flame of powder, exploded in a closed space so that the gases cannot freely expand, is 3340° C. They deny that the solid products are in a state of vapour at this temperature, and conclude that the pressure can never reach 4500 atmospheres, or 30 tons.

Professor Abel considers that the conclusions to which Bunsen and Schischkoff have been led by their elaborate investigation of the products of decomposition of gunpowder are, in the most important respects, so greatly at variance with the views hitherto adopted respecting the general nature of the chemical changes involved in the explosion of gunpowder, and consequently with reference to the several conditions which influence the degree of force exerted by the explosion, that all who are interested in the considerations embraced in the research of these chemists will be inclined to scrutinize closely the means by which they have arrived at their results, before accepting them as representing correctly the effects obtained by the employment of gunpowder in practice.

Major Morgan, the present assistant superintendent of the Royal Gunpowder Factory, considers that all these determinations must be received with caution, and checked by the results obtained by actual experiment. He says that the explosive force of gunpowder has been calculated from the products of combustion, on the assumption that certain laws hold good; but that it must be borne in mind that these laws have been verified only within certain limits of pressure and temperature, and when we come to such very high pressures and temperatures as are met with in the explosion of gunpowder, any conclusions founded on them must be received with circumspection. He is of opinion that the solid products are undoubtedly in a state of vapour at the time of explosion, and quotes Professor Bloxam as well as Piobert and Rumford in support of this view. The following formula he considers may possibly represent the actual state of decomposition before the elements have entered into a second state of combination.

$$12KNO_3 + 20C + 5S = 20CO + 5SO_2 + 6K_2O + 12N.$$

The method of calculating the amount of gas produced, with the temperature and resulting pressure, is as follows:—

Constituents.	Units of Heat evolved.	Products.	Volumes of 46·6 Cubic Inches.	Weight in Grains.	Specific Heat.	Units of Heat required to raise 1° C.
20C.	595.440	20CO.	40	560	·174	97·44
5S.	352,000	$5SO_2$	10	320	·11	35·2
$12KNO_3$.		12N.	12	168	·174	29·232
		$6K_2O$.		564	·174	98·136
Total.....	947,440		62	1612		260

Thus 1612 grains of powder produce 2889·2 cubic inches of gas at 0° C., and 1 atmosphere pressure; and consequently 1 cubic inch, or 240 grains, will produce 430 cubic inches of gas at the same temperature and pressure. The temperature of the products occupying 430 times the powder space will be $\frac{947440}{260} = 3644°$ C.; and the pressure, supposing the solid potash to occupy one-third and the gases two-thirds of the powder space, will be $= \frac{3}{2} \times 430\ (1 + \cdot00366 \times 3644) = 9250$ atmospheres, or 62 tons per square inch.

This is by no means the highest pressure which may be arrived at, seeing that the products may be still further decomposed; for it is well known that at a high temperature carbonic oxide will reduce potash, and the tendency of potassium to pass into vapour is well known. It is possible, therefore, that in the presence of carbonic oxide, and at such a temperature, the elasticity of the two vapours of potassium and oxygen may be sufficient to cause decomposition, and thus we should have all the products in the state of vapour with a corresponding augmentation of pressure.

Another consideration in favour of a possible high pressure, is the limit to which the laws applicable to gases can be carried. At some point the liquid form would be assumed. It is true, as in the case of carbonic acid, that it is impossible to liquefy gases when the temperature is very high; but the pressure may approach the law of liquid pressure, which we know increases with extreme rapidity.

It is necessary to adopt some such reasoning as the above, in order to harmonize the pressures calculated with those which have lately been obtained by actual experiment.

Count Rumford was the first who attempted to obtain the pressure of gunpowder by actual experiment. Not being able to obtain any material strong enough to confine it when exploded in its own space, he measured the pressure when exploded in closed spaces bearing various relations to the bulk of the charge. He made use of a little gun which had no vent, and inclosed the muzzle by a hemisphere which was weighted till the whole force of the generated elastic fluid was just able to lift it, and which in that case counterbalanced, and consequently *measured* its elastic force. The charge was fired by heating the walls of a long narrow chamber at the base of the charge. If quite filled with powder, the capacity of the gun was $25\frac{1}{2}$ grains. The following table gives the actual pressures measured and corrected by Rumford:—

Charge in Grains.	Ratio of Charge to Space.	Pressures in Tons per Square Inch.	
		Measured.	Calculated.
1	·039	0·5	0·5
2	·078	1·2	1·1
3	·117	1·5	1·8
4	·156	2·5	2·6
5	·195	3·7	3·6
6	·234	4·6	4·8
7	·273	5·4	6·2
8	·312	7·8	7·8
9	·351	10·3	9·8
10	·390	12·6	12·1
11	·429	14 8	14·9
12	·468	17·1	18·1
13	·507	21·9	22·0
14	·546	26·7	26·5
15	·585	31·5	31·9
16	·624	47·3	38·2
17	·663		45·6
18	·702	73·2	54·3
19	·741		64·5
20	·780		76 5
25½	1·		194·5

RODMAN endeavoured to measure the pressure of gunpowder as it actually existed in the bore of the gun. One method adopted by him was to swing the gun as a pendulum, and trace the curve it made on a revolving cylinder as it recoiled. He thus calculated that during the first fourth of the time the shot took to traverse the length of the bore, the mean pressure was 8 tons; during the first sixteenth of the same time, it was 16 tons; and during the initial stages of motion it was 22 tons per square inch.

Another method he adopted was by inserting pistons at various points of the bore, and causing these pistons to act on an indenting tool, which was thus forced into a piece of copper. These he called pressure gauges.

He tried what effect varying the size of the bore had on the pressure, with the following results:—

The following table shows the velocity of the shot in feet per second and the pressure of gas per square inch (in tons) due to equal columns of powder behind equal columns of metal, when fired in guns of different diameters of bore, each result being a mean of ten fires:—

Diameter of Bore.	Windage.	Weight of Charge.	Weight of Shot.	Velocity. F.S.	Pressure at Different Distances from Bottom of Bore.						
Inches.	Inches.	Lbs.	Lbs.		At bottom.	At 14″.	At 28″.	At 42″.	At 56″.	At 70″.	At 84″.
7	·07	5·13	74·44	904	16·3	7·1	3·7	2·9	3·1	3·6	3·0
9	·09	8·48	124·42	898	30·0	9·4	7·9	6·7	13·1	9·4	10·2
11	·11	12·67	186·03	927	38·7	13·1	12·4	10·0	12·7	15·1	11·2

The points most worthy of note in these results are the very marked increase in the pressure of gas as the diameter of the bore increases, and that the indications of pressure are greater at 56, 70, and 84 inches than at 42 inches, especially in the 9-inch and 11-inch guns. The former RODMAN accounted for by the greater heat developed in a large than in a small charge. The increase of pressure towards the muzzle, he believes to be due to the more violent and sudden contraction in the thin than in the thick part of the gun. For in the thick part of the gun the pressure is much less rapidly developed, and subsides much more gradually, the contained gas forming an elastic cushion which would, if the bore were long enough, allow this part of the gun to return from its chained to its free condition without any vibration at all; while in the model used in these experiments the pressure is almost instantaneously developed and as suddenly subsides in the chase of the gun. So that while the indenting piston is on its way outward, it is suddenly met by the returning specimen, which is drawn in along with the housing by the contraction of the gun, with such violence as to amount in effect to a smart blow of the indenting tool against the specimen. Close examination showed a number of marks or cuts of the indenting tool on the specimen in this part of the gun, caused by the tool not striking in the same place at each vibration of the gun.

He also tried the effects of varying the size of grains of powder with the following results:—

The table below shows the velocities of shot and pressure of gas due to the equal charges of powder of the same composition, and differing only in size of grain: each result being the mean of five fires with the 11-inch gun, the same shot being used in all the fires—

Diameter of Grain.	Weight of Charge.	Weight of Shot.	Initial Velocity.	Pressure of Gas in Tons.		
Inches.	Lbs.	Lbs.	F.S.	At Bottom.	At 14″.	At 28″.
·6	12·67	186·3	933	9·5	4·6	3·6
·5	"	"	932	9·5	5·0	3·3
·4	"	"	881	11·4	4·8	3·2
·3	"	"	890	15·8	4·8	3·0
·3	"	"	912	29·4	6·6	3·7

The last result shows a pressure considerably greater than those preceding it, and is accounted for by the powder being of less density. These experiments led the way to a great improvement being made in the manufacture of powder for war purposes where large charges have to be used. As the size of ordnance increases the strain of the gun increases to a very great extent, and unless some means had been discovered of moderating the violence of combustion of gunpowder in large charges, it would be impossible to make guns sufficiently strong to withstand the explosive effects. Experiment, however, shows that it lies in our power to vary the rate of combustion of gunpowder, and in this gunpowder differs very much from many of the substances which have been sought

to be used instead of it. In gun-cotton the instability which renders explosion possible is brought about by chemical action, so that atom finds atom in closest proximity ready for combination if only sufficient temperature be attained. In gunpowder, on the contrary, the instability is produced by mechanical mixture, and on a minute scale the particles of charcoal are burned like coals in a fire. With gunpowder in its rude state, the difficulty was to get the particles close enough together to make the combustion sufficiently rapid; and it was not until the importance of thorough incorporation was understood that any real progress was made in rendering it a destructive agent. Even with thorough incorporation it was necessary to provide for the rapid ignition of the various particles, for the combustion could not travel with sufficient rapidity through the entire mass. To make the action energetic enough it was necessary, as it were, to light the fire in a great many places. Granulation effects this by allowing the flame from one point of ignition to spread throughout the charge and ignite all the grains very nearly instantaneously. Thus the action depends on the rapidity of ignition of the grains, and the rate of combustion of each grain. The rapidity of ignition of the grains depends on the size of the spaces between the grains, and the rapidity of combustion on the smallness of the grains themselves; but as these are opposed to one another, we can readily see that with some size of grain which is most favourable to both requirements the combustion of the whole charge will be most rapid. Small grains burn rapidly, but the spaces between them being also small, the ignition in large charges will not be so rapid. Large grains burn slowly, but will admit of rapid ignition. The shape of the grain is another element, but one of still more importance is the density; for if the grain be porous, the flame will not only pass between the grains but will also penetrate into their mass. The most rapid combustion therefore will be obtained by combining a certain size and shape of grain with a certain density, and if the combustion is to be moderated the size of the grain must not only be increased but so must the density, especially in large charges where the pressure is very great.

The objects to be attained in regulating the size and density of the grains of gunpowder to be used in ordnance, are the greatest possible velocity of the projectile, and the least strain on the gun. These cannot be obtained by one set of conditions for all natures of ordnance. A small projectile moves quickly, and relieves the strain in a much greater ratio. A heavy projectile not only moves slowly, but even a considerable motion does not relieve the strain in a proportionate manner, because the column of powder is longer in a large than in a small gun. With small-arms, therefore, small grains and low densities are required, but large grains and high densities with large guns. Owing to the effect of heat and pressure in accelerating the combustion, it cannot be determined *a priori* what size or density of grain will suit any particular gun. These can only be determined practically from the pressures produced in the guns themselves. Following in the footsteps of Rodman, the question of the most suitable powder for ordnance has been taken up by many European governments; and a committee on explosives, under the presidency of Colonel Younghusband, R.A., F.R.S., superintendent of the Royal Gunpowder Factory, Waltham Abbey, has had the subject under consideration in England for some years.

The following pressures and initial velocities have been obtained by them in firing a 180 lbs. shot from an 8-inch gun:—

Nature of Powder.	Charge. Lbs.	Initial Velocity. F.S.	Maximum Pressure. Tons.
R.L.G.,	30	1324	29·8
Russian prismatic,	32	1366	20·5
Service pellet,	30	1338	17·4
Pebble. No. 5. Density, 1·78,	35	1374	15·4

With the 10-inch gun firing a 400 lbs. projectile the principal average results in various series of six rounds each, are shown in the following abstract, the pressure given being the highest as indicated by the crusher gauge, an instrument somewhat similar to Rodman's pressure gauge.

Nature of Powder.	Density.	Charge. Lbs.	Velocity. F.S.	Pressure. Tons.
R.L.G.,	1·742	60	1318	51
	1·733	60	1321	48
	1 67	60	1313	53
Russian prismatic,	1·66	61	1335	19
		68	1425	29
Ritter prismatic,	1·66	61	1349	2·½
		70	1416	24
	1·732	70	1474	29
	1·782	70	1432	21
Pebble,	1·732	60	1359	21
	1·782	60	1298	15
Pellet,	1·677	64	1364	25

R.L.G., or *Rifle Large Grain*, which was the powder in use with heavy guns, is shown by these results to be very unsuitable in large charges. With *Pebble* powder more than 100 feet additional initial velocity can be obtained, while the pressure is reduced to less than half. Pebble powder has in consequence been introduced as the powder for all heavy guns above a certain calibre, the R.L.G. being reserved for the smaller kinds, and for field-guns. It was found, however, when a 35-ton gun of 11·6 inches bore, and firing a 700 lbs. shot was made, that pebble powder was not suitable for such heavy ordnance. The following are the results of proof with this gun:—

Charge. Lbs.	Velocity. F.S.	Pressure. Tons.
75	1163	17
100	1237	25·4
110	1303	31·8
120	1364	46·4
130	1348	63·7

These results led the committee to the conclusion that a new powder must be sought for guns of this

weight, and they still have the matter under consideration.

MANUFACTURE.—The merely mechanical part of the manufacture of gunpowder is essentially the same in principle, and differs only to an immaterial extent in detail, whether in the various gunpowder mills in Great Britain, or in those of her continental neighbours. The writer of this article will trace the method of manufacturing gunpowder as it is employed at the Government Mills, Waltham Abbey, and is so well described in Captain SMITH'S handbook of the manufacture and proof of gunpowder.

Before the ingredients can be mixed, they must be reduced to a powder sufficiently fine for the purpose. It is true that some manufacturers do not pulverize or mix their ingredients at all, but simply weigh out as much of each as is required in lumps and fragments, and throw them on the bed of the incorporating mill. But this clearly involves a loss of time, as the action of the incorporating mill must be at first merely that of grinding and bringing the three ingredients into a just position, before any *incorporation*, properly so called, can be effected. It is important to bear clearly in mind the meaning of the terms *mixing* and *incorporating* as they are used by gunpowder-makers. Though gunpowder is really only a mixture, very intimate no doubt, of the three ingredients, and not a new chemical substance formed out of them, yet by mixing is understood only the stirring together for a few minutes of the saltpetre, sulphur, and charcoal to get them properly distributed amongst each other; and by incorporating, the long-continued trituration and grinding which the mixture undergoes under heavy edge runners, by which a mass of the ingredients becomes transformed from a mere mixture of three different substances into gunpowder. A preliminary mixing, such as is employed at Waltham Abbey and most other gunpowder works, *may* be dispensed with; incorporation, whether performed by pestle and mortar, in the stamping mill, or under edge runners, never.

The saltpetre is used moist, as it comes from the refinery, containing usually from 3 to 6 per cent. of moisture. The sulphur, after being ground under edge runners, is sifted through a slope reel covered with 32-mesh wire.

The charcoal, after being carefully hand picked to guard against the introduction of any fragments of foreign matter and underburnt knots of wood, is ground in a mill resembling a coffee-mill in action. It is most important that before grinding the charcoal after being burnt, it should be allowed to stand for ten days or a fortnight; for when ground fresh after burning, the finely-powdered charcoal absorbs and condenses oxygen so rapidly as to generate enough heat in so bad a conductor as to cause spontaneous combustion. Instances of fires in gunpowder factories from this cause are on record, fresh ground charcoal having been left overnight in wooden bins or covered boxes.

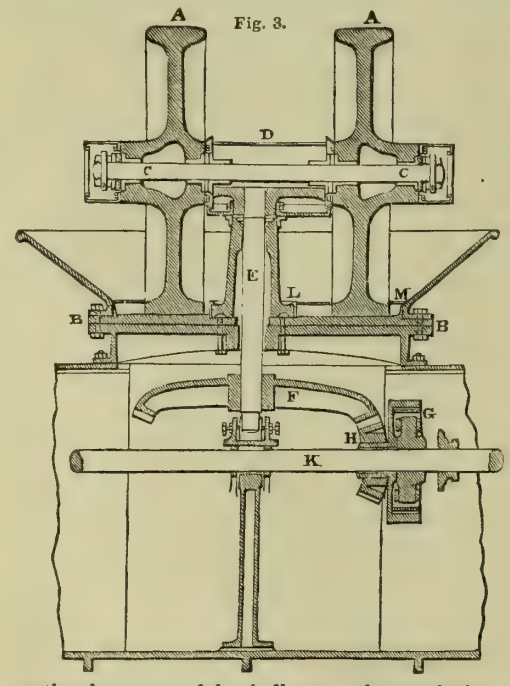
The relative proportions of the three ingredients are weighed out in quantities of 50 lbs.—that is to say, 37½ saltpetre (+ the extra weight for the moisture), 7½ charcoal, and 5 sulphur—and transferred to the mixing machine, which consists of a gun-metal cylinder (phosphor bronze is now used in some mills), traversed in its centre by an octagonal shaft provided with several fan-like arms. Both the shaft and cylinder are kept in motion, but in different directions. This latter arrangement so facilitates the commingling that the homogeneous powder is ready for removal in from five to ten minutes, when it is transferred to bags, which are pressed, and the mouths of which are firmly secured, in order to prevent the disunion or separation of the ingredients in the order of their density during the transport to the incorporating mill. It is evident that if the charges were too lightly packed, the ingredients would be liable to be separated in a greater or less degree, the saltpetre finding its way to the bottom, while the sulphur and charcoal would form layers above—the latter, from its light, pulverulent state, escaping in the form of dust between the fibres of the cloth of which the bag is formed. In this state, though not so easily ignited and slower in burning than gunpowder, it is explosive, more especially in large quantities. The difference in effects may be well illustrated by flashing a small quantity of powder and an equal amount of green charge on thick plates of glass. The former will flash off, leaving no residue, and doing the glass no injury; the latter will puff off slowly, and shiver the glass to pieces from the longer time the heat is applied to it, and will leave the fragments coated with particles of half-decomposed saltpetre and sulphur.

The next process is the *incorporation*, which is unquestionably the most important of all the operations in the manufacture of gunpowder. Upon the thorough and effectual incorporation which it receives depends mainly the excellence of English powder, which is allowed to surpass that of all other nations in strength. Great attention is paid to the process in this country, not only for military, but for sporting purposes, and the most powerful mills are always used. It has been carried to the highest pitch of excellence: some of the finer sporting powders made in this country are said to be incorporated for twelve hours. A chemist who has to unite two or more powdered substances as closely as possible places them in a mortar, and works them round with the pestle for a length of time, trusting more to the rubbing and twisting action of the pestle than to stamping. The gunpowder-maker endeavours to imitate this rolling and grinding together on a large scale; and finds by experience that the most effectual way to do so is to grind the materials together under heavy edge-runners of stone or iron, which by their motion, a compound of rolling and twisting, soon works them into a homogeneous mass. The old stamping mills, in which the ingredients were subjected to long-continued stamping under pestles working in small mortars, have been out of use for many years in this country, though they are still employed in France and in other continental countries. The action of such mills has very little

incorporating effect, and is, moreover, attended with even more risk than the mills used in this country. The same remark applies to the *moulins à tonneaux*, in which a partial incorporation is effected by placing the material in a revolving barrel or drum, along with some large metal or wooden balls. Such mills are much used abroad for pulverizing the ingredients, and occasionally for incorporation; but the fact is now generally admitted that the most effectual and speedy incorporation can be obtained with mills of the description now universal in England, and their employment is becoming general on the Continent.

The incorporating mill consists of a pair of large heavy edge-runners, A A (see Fig. 3), of iron or stone, weighing about 4 tons each, which revolve on a strong circular bed, B B, of the same material. The faces of the runners are nearly flat, with a slight bevel towards the edge. The runners are connected

Fig. 3.



together by a powerful spindle, C C, of wrought iron, which rests in brass bushes placed in the cross-head, D, so as to allow the spindle and runners to rise and fall according to the thickness or thinness of the layer of material on the bed. The spindle is placed on the cross-head, so as to bring one runner nearer to it than the other, and therefore to cause them to describe different paths when in motion. The cross-head is fixed on a vertical shaft, E, on which is fixed, underneath the flooring of the mill, a wheel, F, driven by a friction clutch, G, and pinion, H, on the driving shaft, K, which passes under the whole group of mills. By this arrangement the whole of the machinery is kept underneath and out of reach of damage from explosion. The cross-head is fitted with a bracket on each side to carry a *plough*, or wedge-shaped piece of wood shod with felt and leather, which travels round on the bed immediately in front of the runners, and thus keeps the composition from working away from them. The bed has a curb or edge round the outside and inside of the circular path described by the runners, that on the outside, M, being formed by a sloping rim or casing fixed all round the bed, that on the inside, L, by the circular base of the cheese, O, or conical socket, down which the vertical shaft of the cross-head passes. Both the outside and inside curbs have gun-metal rings round them for the plough to work against.

The charge (either a *green* charge from the mixing house, or a dust charge from the dusting house or granulating house), having been previously carefully sifted, is thrown upon the bed of the mill, carefully raked so as to form a bed of uniform thickness, and watered with about 2 pints of distilled water to insure the intimate cohesion of the particles. The runners are then moved round a quarter revolution, and the piece of the mill cake left under the runners from the former charge is broken up and distributed over the fresh charge. The runners are then started at a speed of about eight revolutions a minute. More water is added from time to time, the amount depending very much on the state of the weather. From 2 to 3 pints are generally found to be sufficient in very damp weather, but as many as 8 or 10 are necessary on very bright days. The process is continued for a green charge about three hours for common powder, and as much as eight hours for powder for small arms.

Gunpowder leaves the incorporating mill partly in the state of soft cake, and partly dust. The cake may be broken up into grains, as is done in many countries, but such grain is too soft to stand much handling or transport without crumbling to dust. To insure uniformity and good keeping qualities, powder must be converted into firm grains. The *corning* or *graining* of gunpowder has been recognized as one of the most important features in the manufacture from a very early period. The earlier makers probably damped the incorporated materials till they acquired a certain consistence, and then forced the mass through sieves, thus forming granular fragments, which were afterwards hardened by drying. Strange though it may appear, powder is made in this fashion in some out of the way places in England at the present day. There is no difficulty in forming good hard grains in the manner described, but a little reflection will show that it is at the sacrifice of the incorporation which has been previously effected. The moisture added partly dissolves the saltpetre, which in drying forms a hard external surface to the grains.

The only perfect way of converting gunpowder into serviceable grains without in any degree whatever interfering with the perfect incorporation of the ingredients, is first to compress the soft material into hard masses by pressure alone, and then to crush or cut up these masses into the description of grain required. The object of pressing, then, is to convert the soft dusty mass of incorporated ingredients, now gunpowder, into hard cakes of the

particular density which is found to give the best results when the powder is finished; when once the cakes are formed, they can be subsequently broken up by various contrivances into grains of any size, all of which will have an uniform density and hardness, and which can be freed from dust, and glazed and polished so as to bear handling and transport without breaking or crumbling.

Gunpowder is generally pressed in layers between plates of gun-metal, or copper, in an hydraulic press, though screw presses are still in use in many factories. The thickness of the cakes depends on the nature of the powder to be produced, that for fine grain is about three-eighths of an inch in thickness. In order that the powder may be conveniently and uniformly arranged for pressing, it must undergo a preliminary process of *breaking down*. This is done by passing the mill-cake through a machine which consists of two pairs of gun-metal grooved rollers, the first pair being rather more widely set than the second, and one roller of each pair works in a sliding bearing, and is held at a proper distance from the other by a weighted lever. This arrangement admits of each pair opening out a little if too large a quantity of the cake is drawn in between them.

It is a matter of considerable difficulty to insure uniformity of results in pressing powder. It is of the highest importance that the density obtained should be uniform, because the qualities and explosive effects are materially affected by comparatively slight variations in density. A difference of ·05 in the density of the charges may affect the initial velocity of a 12-lb. shot, fired with a 1-lb. charge, to the extent of about 50 feet a second; and yet no difference between the two powders may be perceptible, and they may be undistinguishable from each other by any ordinary test.

The density of powder is taken in the mercury densimeter, by putting a given weight of powder in a glass globe and filling up the remainder of the globe with mercury. A comparison of the weight of the globe thus filled with the weight when completely filled with mercury, gives the means of calculating the density. In order that the experiment may be accurately made, the air must be exhausted before the mercury is allowed to enter, otherwise bubbles of air would adhere to the powder and interfere with the correctness of the result.

There are two ways in practice of obtaining the proper density in the press-box. The first is by the gauge attached to the pump, which shows at any moment the actual pressure per square foot and square inch on the cylinder of the press. The other is by observing the *effect* of the pressure applied; that is to say, the extent to which the contents of the box have been compressed, as shown by the distance to which the block has been forced into the press-box. If equal pressure had equal effects on gunpowder meal, there would be no difficulty in obtaining any particular density, for the escape-valve of the hydraulic press could always be arranged so as to stop the action of the press when a certain pressure has been reached. The meal, however, possesses varying degrees of elasticity and resistance to pressure, depending to a great extent on the moisture it contains, and the state of the atmosphere at the time. A pressure of 70 tons per square foot may therefore be applied to the contents of the press-box, and the press cake, when dried and examined in the densimeter, may show a density of 1·74. The next pressing made, as far as can be judged, under exactly the same circumstances, may have a density as low as 1·64, in consequence of the elasticity of the meal refusing to yield to compression. The safest rule to go by is therefore the distance, and in practice this method is found to give the best results.

It is found in practice at the Royal Gunpowder Factory that though absolute uniformity cannot be guaranteed in pressing, very tolerably close results can be obtained by mixing the powder during manufacture according to the different densities, as shown by the densimeter. Thus, if R.L.G. be in hand and the density fixed be 1·67, a mixture of two powders which are estimated to produce respectively when finished 1·64 and 1·70 will be found to give the required density.

The great importance of density has been already mentioned. It has received the greatest attention of late years in the manufacture of gunpowder in this country. An example may be given of the effects produced in the same gun under the same conditions except density. The Committee on Explosives, firing 70 lbs. charges in a 10-inch gun with a projectile weighing 400 lbs., obtained the following results:—

Pebble Powder, of density,	Velocity at 400 yards from the muzzle. F. S.
1·84	1288
1·78 — 60 lbs. } 1·81 — 10 lbs. }	1424

Were such discordant velocities allowed to exist in the same gun in practice, it would be impossible to produce results in proportion to the accuracy of practice which is attained with the arms of precision of the present day. We accordingly find that all powders manufactured are required to be of a certain standard as regards density and velocity.

Density plays another important part in powders used for small arms. It has been found that powders of low densities are apt to foul the rifles, while powders of high density are free from this defect.

The next process in the manufacture of gunpowder is the granulation, or breaking the press-cake, after it has been made of the required density, into grains of the size and form calculated to give the best results in practice. The powder used with heavy guns is called "pebble powder," on account of the size and shape of the grains. Each grain is as nearly as possible a cube five-eighths of an inch in length of side, but having the edges and corners rounded off to prevent as much as possible its breaking up into dust in transport. To obtain these cubes an ingenious machine has been contrived at the Royal Gunpowder Factory, which cuts up the press-cakes,

which are five-eighths of an inch thick, first into strips 16 inches long and five-eighths of an inch square in section. These strips are again cut up in the same machine into little cubes. Smaller grain powders are made by being broken up from press-cake in a machine of a different character. The press-cake is about five-eighths of an inch in thickness, and is first passed through a pair of rollers at the top of the machine, which are furnished with large teeth. The broken powder falls on a sieve of a mesh regulated to the size of the powder. This sieve is kept in a constant state of jolting, so as to cause the finer grains to pass through, and allow the larger grains to pass on to a second pair of rollers, which breaks them up smaller. The same process is repeated through a second, third, and fourth pair of rollers. A long screen of a finer mesh passes underneath the whole, which takes out the dust and finer grains. The grains of the required size pass into boxes running on wheels and rails.

The following are the different sizes of the smaller grain powders in use in Her Majesty's service :—

1. L.G. (or large grain) ; size, 8 to 16 mesh.
2. F.G. (or fine grain) ; size, 16 to 36 mesh.
3. R.L.G. (rifle large grain) ; size, 4 to 8 mesh ; density, 1·68.
4. R.F.G. (rifle fine grain) ; size, 12 to 20 mesh ; density, 1·6.
5. R.F.G.^{2} (for Martini-Henry rifle) ; size, 12 to 20 mesh ; density, 1·735.

In the trade, sporting powders are distinguished by numbers, thus—

No. 1,	40 to 72 mesh.
No. 2,	28 to 40 "
No. 3,	24 to 28 "
No. 4,	20 to 24 "
No. 5,	17 to 20 "
No. 6,	14 to 17 "

Blasting powders vary very much in size of grain. Some are as large as from 2 to 4 mesh, and others as fine as from 20 to 36 mesh.

The granulated powder as it comes from the machine contains amongst it a large quantity of dust. This is formed by the crushing action of the granulating machine, and the grain in this condition is not to be made use of as powder, being rough and porous on the surface, and very angular in shape. The presence of a large quantity of fine dust would not only render it most inconvenient to handle in magazines or elsewhere, but would also render it more liable to absorb moisture and to deteriorate. A rough, unpolished angular grain would very speedily rub down into dust if subjected to much shaking in transport. The object of the gunpowder-maker is therefore first of all to free the granulated powder from all traces of dust, and secondly to polish or give a surface to the grains themselves, to enable them to bear a great deal of friction without deterioration.

Powder is freed from dust by placing it in revolving *reels* covered with cloth or wire mesh of various degrees of fineness, through which the dust escapes. It is *glazed* by causing the grains to rub against each other in revolving wooden barrels or churns. The extent to which the operations of dusting and glazing can be carried, and the nature of the appliances used, depend on the density, hardness, and size of grain of the powder operated on. A large-grained, dense, and hard powder will bear a great deal of knocking about in the reels without becoming disintegrated and forming fresh dust ; and will, moreover, bear a great deal of friction in the glazing barrels, acquiring speedily a high degree of polish. But the case is quite different if a small-grained soft powder of low density be operated on. In the latter case the dusting must be carefully conducted, or the process will develop as much fresh dust as it removes ; and the amount of friction the grains will bear in glazing without simply rubbing away to nothing must be likewise carefully regulated.

It is found in practice that powder may be divided into two classes, each of which requires different treatment in dusting and glazing—namely, the *cannon powder* of all classes, made with alder or willow charcoal ; and the *small arm powder* of all classes, made with dogwood charcoal. The former class of powder is not only pressed to a higher density, but is made of a larger size of grain ; the latter is generally of lower density, and of much smaller size.

There are two classes of dusting reels in use—the slope and the horizontal. Slope reels are used for fine grain powder, which passes through in a continuous stream, but does not remain in the reels in large quantities at any one time, so as to crush up the grain unnecessarily. Horizontal reels are used for larger grained and denser powders, where larger quantities may be put in at a time.

The following table may be taken as a specimen of the processes through which the powders go at the Royal Gunpowder Factory after leaving the granulating machine up to the time of finishing and packing in barrels :—

	R.L.G.	R.F.G.
1st Dusting,	In a horizontal reel covered with 24-mesh canvas, making 40 revolutions a minute for half-an-hour.	Run through a slope reel covered with 24-mesh canvas, making about 40 revolutions a minute.
Glazing,	In wooden barrels making 34 revolutions a minute for 40 minutes, with ½ oz. graphite per 100 lbs.	In wooden barrels making 34 revolutions a minute for five and a half hours.
2nd Dusting,	In a horizontal reel covered with 24-mesh canvas, making 40 revolutions a minute for half-an-hour.	Run through a slope reel covered with 28-mesh canvas, making about 40 revolutions a minute.
Stoving,	Same for both.	
3rd Dusting, or Finishing,	Not required.	In a horizontal reel covered with 28-mesh canvas, making about 45 revolutions a minute for twenty-two hours.

The powder is dried in large chambers heated by steam pipes, and is spread out on trays which contain about 16 lbs. each. It is thus exposed to a temperature of about 125° Fahr. for 24 hours. Pebble powder requires a longer time and a higher temperature for its efficient drying, on account of its larger grain and greater density.

When finished, gunpowder is packed in barrels containing 100 lbs. each. Pebble powder, owing to its greater density and compactness, is packed in barrels of 125 lbs.

Before being passed into the service, all powder undergoes a rigid examination and proof, which has for its object to ascertain—

1. If the powder have a proper colour to the eye, a proper amount of glaze, a sufficiently hard and crisp texture, and if it be free from dust and perfectly clean.

2. If it be properly incorporated.

3. If the grains be of the proper size and shape, and if the different size of grains present be in the proper proportion.

4. If the powder be of the proper density.

5. If the action of the powder when fired be uniform, and up to a fixed standard.

6. If it contain the proper proportion of the ingredients.

7. If it possess a sufficient power to withstand the absorption of moisture.

No. 5 is considered the most important point, in order that the practice obtained on service may be always relied on. Within the last few years a rigid proof has been established in the arm with which the powder is to be used. Thus R.F.G. is proved in the Snider Enfield rifle; R.F.G.^{2}, in the Martini-Henry rifle; R.L.G., in a 9-pounder field gun; and pebble, in an 8-inch rifled gun.

The velocities obtained are as follows:—

R.F.G.,	1270 f.s.
R.F.G.^{2},	1310 "
R.L.G.,	1410 "
Pebble,	1450 "

Properties.—Good powder, according to Abel and Bloxam, should be perfectly uniform in texture; light specks or glittering points indicate an incomplete mixture. The grains should be sufficiently hard not to be easily crushed between the fingers, and not to soil these or a piece of paper by mere contact. Gunpowder should burn rapidly, leaving only a *very slight* residue. If inflamed upon white paper, it should blacken it but slightly, and should on no account set fire to it. Powder is inflamed by any burning substance, by an electric spark, by red-hot metal, or by violent concussion. It does not ignite, however, by exposure to a temperature below redness. If subjected in an atmosphere of hydrogen or carbonic acid to a gradual increase of temperature, the sulphur may be completely separated, subliming upon the cool portion of the vessel.

It has been proved that powder may be inflamed, not only by the concussion of hard bodies, but by that of comparatively soft ones, provided it be sufficiently powerful. Experiment has shown that powder placed upon lead, or even upon wood, may be ignited by the shock of a leaden bullet fired at it.

No doubt the inflammability of a powder is greatly influenced by its physical state. A fine-grain powder will burn much more rapidly than powder of a larger grain. The greater the density, the more gradual is its combustion. Angular powder will burn more speedily than the round-grained, and the inflammability of powder is not only retarded by the presence of moisture, but also by the glazing.

Powder in which the theoretical proportions are exact, and in the manufacture of which a very inflammable charcoal has been used, the ingredients having been mixed without the application of very great pressure, will undergo, when ignited, an almost instantaneous decomposition. Such a composition, in many respects, resembles the fulminates; the strain which it exerts upon the fire-arm is far too powerful; hence it is not so generally applicable as a more gradually disintegrating mixture.

Gunpowder always attracts more or less moisture, since charcoal, however dense, absorbs humidity from the air; though, of course, the hygroscopic property of powder is considerably increased by the use of porous charcoal in its manufacture, or by the presence of any considerable quantity of powder-dust. Powder, manufactured with perfectly pure saltpetre, is found, if preserved in dry stores, to absorb about 0·5 per cent. of moisture; the amount naturally increases considerably if it is kept in a damp situation. Fine-grain powder is generally found to absorb moisture more rapidly than the large-grained.

The amount of ash left upon the ignition of gunpowder varies according to the purity of its ingredients, the proportions employed, and, more particularly, the nature of the charcoal used. Its gradual accumulation in a fire-arm is a source of great inconvenience, since it soon renders it foul and difficult to charge, thus limiting the number of rounds that can be fired in rapid succession, without cleaning out the instrument. This *fouling*, as it is termed, is avoided to some extent by the use of a small quantity of some fatty substance, which lubricates the barrel, and by preventing the adhesion of the ash promotes its expulsion by the gases as they make their escape.

Bishop affirms that gunpowder explodes exactly at the temperature of 600° Fahr. When exposed to a heat of 500°, its nature becomes totally changed; not only is the whole of the moisture expelled, but the saltpetre and sulphur are reduced to the fluid state. The powder on cooling is found to have changed from blackish-grey to an intense black; the grain has become extremely indurated, and by exposure even to very moist air, it then suffers no alteration by imbibing moisture.

Analysis.—The following is the ordinary method of analysing gunpowder:—

The water is first estimated by submitting a small portion, say 3 or 4 grammes of the sample to be examined, to a temperature of 140° Fahr. in a dessicator until it ceases to lose weight. Some chemists prefer placing a known quantity over sulphuric acid *in*

vacuo, but this method takes much more time, and the former is sufficiently accurate for all ordinary purposes. The loss after drying shows the amount of moisture in the sample, from which the percentage may be readily calculated.

It may be as well to remark here that the quantity of water should be *a mere trace*, if any. If it is found to contain several per cent. of water, it may be rendered again perfectly good by careful desiccation.

The next step is the determination of the nitrate of potash, which is effected by boiling the powder in which the humidity has been determined in about six times its weight of water; the residuum is then carefully collected on a tared filter, washed with tepid water until a few drops of the filtrate when evaporated upon platinum foil give no residue; the insoluble matter upon the filter being then desiccated at 212°, and weighed, the loss will indicate the amount of nitrate of potash. The saltpetre may also be determined by evaporating to dryness the filtrate obtained as above, fusing the residuum at a low temperature, and then ascertaining its weight. Both these methods may be employed, the one thus furnishing a check upon the other.

The nitrate may also be estimated with sufficient accuracy for ordinary purposes by means of a hydrometer, so constructed as to indicate the percentage of saltpetre when floated in water containing a known quantity of gunpowder in solution.

Should the saltpetre contain chloride of sodium, as it ordinarily does, the amount of it may be determined as follows:—The dry and weighed residuum, procured as just described, is redissolved in water, and a little nitric acid and a weak solution of nitrate of silver added, when, if chlorides are present, a curdy precipitate of chloride of silver occurs; this is collected on a filter, well washed, dried, fused with great care in a porcelain crucible, and weighed. One gramme of the chloride of silver represents ·407 chloride of sodium, or ·247 of chlorine.

The amount of sulphur and carbon, respectively, may be ascertained by various methods.

One of these, devised by GAY-LUSSAC, consists in igniting in a platinum crucible a known quantity—say 1 gramme—of the gunpowder, with the same weight of potassium carbonate and of potassium nitrate, and four times the quantity of common salt; by this means the sulphur is oxidized into sulphuric acid, and may be determined as under:—The fused mass, which should be perfectly white, is dissolved in water, and acidified by means of hydrochloric acid. The solution is next filtered, and chloride of barium added so long as a deposit is occasioned. After some time, when the precipitate has subsided, the whole is filtered, and the barium sulphate washed with hot water, until sulphuric acid causes no turbidness in a portion of the washings. The precipitate is next dried, and then, as much of it as is possible being detached from the filter paper, the latter is burned in a platinum crucible until the whole of its carbonaceous matter is destroyed; the precipitate is then introduced, heated to redness, and weighed.

Or oxidize 1 gramme of the powder in a small flask with a concentrated solution of potassium permanganate, adding the latter from time to time till the violet colour remains. Add hydrochloric acid, heat till evolution of chlorine ceases, dilute, and precipitate the sulphuric acid with barium chloride as before (FRESENIUS).

Some chemists digest the residue of sulphur and carbon, after extraction of potassium nitrate, with a mixture of sulphide of carbon and ether. The sulphur enters into solution, leaving the carbon behind; the latter is then washed with sulphide of carbon and ether, dried and weighed, the sulphur being determined by difference; or, the solution may be evaporated to dryness, and the sulphur directly determined.

The percentage of moisture, nitrate of potassium, and sulphur being calculated, the difference indicates the amount of carbon.

FRESENIUS recommends determination of the charcoal by digesting a weighed portion of the powder repeatedly with ammonium sulphide till all the sulphur is dissolved, collecting the charcoal on a filter, and drying it at 212° Fahr., after washing with ammonium sulphide and distilled water.

GUTTA-PERCHA.—This substance is the concrete juice of the Isonandra Percha or Taban Tree (*Isonandra gutta*, HOOKER), growing abundantly in Singapore, Borneo, and other islands of the Eastern

Fig. 1.



Archipelago. The tree belongs to the natural order *Sapotaceæ*, sub-class *Corollifloræ*, and attains a growth of from 2 to 3 feet in diameter, with a height of from 60 to 70 feet. The trunk is straight, the leaves alternate, their upper surface of a pale green, and their under covered with a close, short, reddish-brown hair. The flowers are axillary, from one to

three in the axils, supported on short curved pedicels, and are numerous along the extremities of the branches. The wood is described by Hooker as peculiarly soft, fibrous, and spongy, pale-coloured, and traversed by longitudinal receptacles of reservoirs filled with the gum, forming ebony-black lines. Fig. 1 is a portion of a branch of the gutta-percha tree, exhibiting also the leaves, flowers, and fruit.

The tree flourishes most luxuriantly on alluvial tracts of land lying at the base of hills, where the peculiar character of the soil and comparatively sheltered position appear to favour its growth. On the first introduction of gutta-percha into commerce, the tree was so plentiful in some places that it formed the greater part of the jungle; but it has since become much scarcer, in consequence of the wholesale felling of the trees which was practised, in the first instance, by the Malayan natives.

Historical Notice.—Gutta-percha appears to have been introduced as an article of curiosity into Europe some time prior to its receiving any useful commercial applications. It was first known in England in the days of Tradescant, a native of Holland, who came to reside in this country during the reign of Charles I. It also appears to have been frequently brought from China and other parts of the East in the form of sticks, whips, and other trifling articles. The merit of its first introduction into Europe for purposes of practical utility is divided between William Montgomerie, a Scotchman, who was for some years assistant-surgeon to the Residency at Singapore, on the Malay peninsula, and Sir Joze d'Almeida, who had for many years been resident in the same settlement. This last-named gentleman came over to England in the beginning of the year 1843, bringing several samples of the gutta-percha with him; and, among other channels of communication with the scientific world, had the honour of presenting specimens to the Royal Asiatic Society, for which he received their letter of acknowledgment and thanks. On the whole, however, the merit of priority of discovery seems by general assent to be assigned to Montgomerie, who in point of fact was not only the first European who discovered the value of the product, but the first who exerted himself actively and successfully to bring it into general use. Before the attention of this gentleman was directed to it, it was not only quite unknown to Europeans in general, but was known as an article of value only to a few of the inhabitants even of those localities in which it was produced, and was applied by the natives to very trifling purposes; being chiefly employed to make handles for *parangs* or wood-choppers, as a substitute for wood or buffalo-horn.

The valuable qualities of the substance were no sooner publicly announced than it came into general demand. Its singular adaptation for an infinite variety of purposes was quickly recognized, and an extensive trade in it sprang up almost immediately. In the year 1844, previous to which even its name was unknown to European commerce, 2 cwts. of gutta-percha were shipped experimentally from Singapore. In 1845 the exportation of it from that port rose to 169 piculs, a picul being equivalent to 133·3 lbs.; in 1846, to 5364 piculs; in 1847, to 9296; and in 1848, to 12,000. The whole of this was sent to England, with the exception of 15 piculs to Mauritius, 470 to the Continent of Europe, and 922 to the United States.

The knowledge of the increasing value of the material stirring the avidity of the gatherers spread from Singapore, northward as far as Penang, southward along the east coast of Sumatra to Java, eastward to Borneo, where it was found not only at Sarawak, but also at Brunė and Pontianak on the west coast, and at Reti and Passir on the east. This eager demand for the valuable gum, animated by the thirst for immediate gain, was productive of a reckless destruction of the trees which produced it, which in place of being simply tapped, as in the case of caoutchouc, were felled to the ground, stripped of their bark, and the milky juice collected. Not more than 20 or 30 lbs. could be procured in this way from each tree, and in the course of little over three years as many as 270,000 trees had been thus destroyed. Fortunately for the continued supply of gutta-percha, an English company embarked a large capital in promoting the tapping instead of felling of the trees, and thus prevented an otherwise inevitable failure in the supply of the material.

Extraction and Inspissation of the Juice.—The sap which contains the gutta-percha circulates between the bark and the body of the tree, in vessels the course of which is well marked by black longitudinal lines upon the wood. The juice is obtained either by felling the tree at once, close to the root, and cutting rings in the bark at a distance of from 12 to 18 inches apart, or by simply cutting notches here and there in the living tree in its natural state, in which case judicious treatment will insure a yield from the same tree for many consecutive years without apparent injury. In either case the milky sap which exudes is collected in the shells of cocoa nuts, the spathes of palm leaves, or similar receptacles, where it coagulates shortly after being collected. It is, however, stated by Dr. Oxley, that the coagulation has to be subsequently effected by the natives by boiling the liquid, so as to drive off the aqueous portion. The necessity for this heating of the juice doubtless only occurs when its collection is comparatively rapid, as is the case when the sap is obtained by felling the trees; where, however, simple tapping is resorted to, the exudation of the sap and its collection is no doubt slower, and a partial evaporation occurs sufficient to insure its subsequent coagulation spontaneously. The juice before becoming completely solidified is kneaded by the natives into compact oblong masses, from 7 to 12 inches in length by 4 or 5 in thickness. Gutta-percha arrives now into this country in the form of small slightly-flattened cakes, which are generally either round or square. There are three distinct qualities recognized. The purest is of a yellowish colour and fibrous nature; the second quality much resembles the first in character, but is not quite so tough, and of a slightly reddish colour; while the

third variety is friable, slightly sticky, and of a whitish colour; this last quality is generally covered over with the better class material.

Physical and Chemical Characteristics.—Gutta-percha in a pure state is nearly white, but in the condition in which it occurs in commerce, after having been treated for the separation of mechanical impurities, is of a reddish-brown hue. At ordinary temperatures it is a tough, inelastic substance, possessing about as much tenacity as thick leather, but with rather less flexibility; heated to about 50° C. it softens, and at temperatures of about 70° becomes plastic and capable of being moulded into any required shape, which it retains on cooling: at a slightly higher temperature its ductility is such that it may be drawn into thread or extended to thin sheets with the greatest facility. It is this property of gutta-percha, of becoming plastic and ductile under the influence of a moderate heat, that renders it so admirably adapted to such a variety of commercial purposes, while the faithful reproduction of the most minute details of a mould have rendered it of especial value for modelling and electrotyping. At a temperature of 116° C. gutta percha melts to a transparent liquid, and the heat being raised to a still higher degree, the liquid boils and decomposes, yielding an oily distillate, which is at first nearly colourless, but towards the end of the distillation acquires a brownish-orange hue. Gutta-percha which has once been overheated does not regain its original properties on being cooled to ordinary temperatures, but remains as a sticky, adhesive mass. This may be well observed by setting fire to a strip, when it burns with a bright flame, similar to that of sealing-wax, at the same time emitting sparks and dropping a black adhesive residuum. The specific gravity of the commercial article is about 0·975, being slightly lighter than water; but the density somewhat varies with the conditions of the material, being greatest in those specimens that have been rolled into sheets by the pressure of heavy rollers. The varations in density are no doubt mainly due to a natural porosity, which it is stated may be well seen by examining a thin film which has been obtained by the evaporation of the solution of the material in carbon disulphide under the microscope, when numerous small holes or cavities will be observed. It is due to this porosity that gutta-percha appears to possess a less density than that of water, for if strips of the material are stretched under strong pressure, and immediately cut into pieces under water, the fragments fall to the bottom of the liquid; it also becomes specifically heavier by simple long-continued exposure to air, but this is no doubt due to the increased density of the oxidation products then formed. The porosity of gutta-percha is said to be the principal drawback to its more extensive employment for the construction of bottles and other vessels for holding fluids. It is curious, however, that after having been forcibly stretched the porosity is considerably diminished and a fibrous texture developed; and it will then support without fracture the action of a force equal to double that required for its elongation in the first instance; but although becoming stronger by this treatment in the direction of elongation, it becomes at the same time less able to support any transverse strain.

Gutta-percha is a bad conductor of both heat and electricity. It becomes negatively electric when rubbed, and in the dry state is equal to shellac as an insulator; it is this last property which renders it so extensively employed for the insulation of submarine and subterraneous telegraph wires, for which purpose it was first proposed by Faraday in 1847.

Common gutta-percha is completely insoluble in water, and is not acted on by any sort of saline solution, fermented liquors, dilute acids, or strong alkalies. Concentrated nitric and sulphuric acids, however, attack it, the former with comparative rapidity, the action being accompanied with effervescence, and the evolution of red fumes of nitrous acid; the gutta is eventually disintegrated and acquires a brownish-red colour, becoming doughy and subsequently solidifying to a friable mass. Sulphuric acid acts on it somewhat more gradually, but eventually disintegrates it, becoming itself, at the same time, decomposed with evolution of sulphurous acid. Strong hydrochloric and dilute hydrofluoric acids are stated by Miller to be without action on gutta-percha; but Payen states that the former acid, in its concentrated condition, has a certain slow action ending in converting the material into a brown brittle mass, soluble in alcohol and benzol. Chloroform and carbon disulphide appear to be the best solvents for gutta-percha; the solution takes place with facility in the cold, and is unaccompanied with the preliminary swelling of the material which always takes place when caoutchouc is similarly treated.

By frequent solution, filtration, and evaporation, gutta-percha may be obtained almost white; in this condition it is considerably more flexible than the material in its crude state, and in its physical appearance much resembles white wax, with the exception of being more transparent. Benzol, oil of turpentine, and coal-tar naphtha also dissolve gutta-percha with the aid of heat, but on cooling the solutions become more or less gelatinous, and the addition of alcohol precipitates the material in a pure form; olive oil is likewise a partial solvent with the aid of heat. The change which gutta-percha undergoes when exposed to air and light, and which is familiarly termed "perishing," has been the main drawback to its more extensive utilization for a number of purposes for which it is in all other respects admirably fitted. When exposed to the direct action of solar heat it experiences a sort of doughy fusion, but when placed in situations where it is subjected to ordinary conditions of light and air it gradually changes from the exterior to the centre, exhaling a peculiar acrid odour, and becoming eventually transformed into a hard brittle mass. This change is evidently due to oxidation, as a chemical examination of the altered material proves.

The results of Payen's experiments on the chemical constitution of gutta-percha show it to be composed

of three distinct principles, which were termed by him "gutta," "albane," and "fluavile." Gutta is insoluble in alcohol whether cold or boiling; albane dissolves in boiling alcohol, but is not soluble in the cold liquid; while fluavile is soluble in cold alcohol. PAYEN treated the gutta-percha in thin sheets with boiling alcohol, which dissolved out the albane and fluavile, leaving the pure gutta behind. On cooling the solution thus obtained and allowing it to stand for some time, the albane crystallized out, while the evaporation of the residual liquid gave the fluavile. The average percentage composition thus obtained was as follows:—

Gutta,	78 to 82	
Albane,	16 to 14	
Fluavile,	6 to 4	
	100	100

The pure gutta resembles ordinary gutta-percha in its appearance and characteristics, with the exception of being slightly more flexible at ordinary temperatures. Albane is a white pulverulent mass, soluble in oil of turpentine, benzol, carbon disulphide, ether, chloroform, and boiling alcohol; it begins to melt at 100°, is perfectly fluid at between 175° and 180°, and contracts strongly on cooling. Fluavile is yellow and resinous, dissolving in the same solvents as albane, but differing by its solubility in cold alcohol; it becomes pasty at 50°, and completely liquefies at from 100° to 110°, and at higher temperatures boils and decomposes.

According to the more recent researches of OUDEMANS (Rep. Chem. app. 1, 455) and of BAUMHAUER (J. pr. Chemie, lxxviii. 277) it appears that the true view of the composition of ordinary gutta-percha is that of regarding it as a mixture of a pure hydrocarbon, gutta, isomeric with oil of turpentine, $C_{10}H_{16}$, with oxidation products $(C_{10}H_{16})_2O$, and $C_{10}H_{16}O$, representing the albane and fluavile of PAYEN. Other oxidation products are also present in minor quantities, among which may be included formic acid. This view of the composition of commercial gutta-percha is corroborated by the experiments of C. GREVILLE WILLIAMS, who obtained from the destructive distillation of the material products resembling those obtained under similar conditions from caoutchouc, and mostly polymeric hydrocarbons, isoprene, C_5H_8, caoutchin, $C_{10}H_{16}$, and hevene, also probably polymeric with the two others. The caoutchin forms about 20 per cent. of the crude distillate, and the isoprene about 5 per cent. The special circumstance, however, bearing on the constitution of the original material, was that, besides the hydrocarbon substances already named, the aqueous distillate which was at the same time obtained, instead of being alkaline, as in the case of the destructive distillation of caoutchouc, was strongly acid, from the presence of a volatile organic acid, apparently one of the lower members of the series, $C_nH_{2n}O_2$.

MILLER'S researches (Chem. Soc. J. (2) iii. 273) assigned the formula $C_{20}H_{30}$ to pure gutta, which would correspond to a percentage composition of carbon 88·99 and hydrogen 11·11. He found ordinary gutta-percha to have the following percentage composition:—

Hydrocarbon.	Resin.	Woody fibre.	Water.	Ash.
79·70	15·10	2·18	2·5	0·52 = 100

There is but little doubt that this resin, regarded as an oxidation product derived from the pure gutta, is formed at the time the juice is being withdrawn from the trees; a more careful method of collection would probably yield a purer article containing a larger percentage of gutta and correspondingly diminished amount of oxidation products. The so called "perishing" of gutta percha is evidently a slow oxidation process, by which the percentage of gutta is reduced *gradatim*, and by which it is simultaneously transformed into resinous products containing oxygen. This change, as has already been remarked, occurs with more or less rapidity when gutta-percha is simultaneously exposed to air and light; but under circumstances where these conditions are absent the material may be preserved for almost an indefinite period without appreciable change. It is for this reason that gutta-percha continues to be of such immense service in coating metallic wires for purposes of insulation, as for instance, in the construction of submarine telegraphic cables. The changes which gutta-percha experiences on exposure to air have been studied by HOFFMAN, who found the altered material to consist of a brown fragile mass from which cold alcohol extracted a brittle substance having a percentage composition of carbon 62·8, hydrogen 9·6, and oxygen 27·9. By the further action of boiling alcohol a substance of similar physical characteristics was procured, having a composition of carbon 67·7, hydrogen 10·1, and oxygen 22·2. The residue from these operations consisted of unaltered gutta, which has been already seen to be composed of carbon 88·99 and hydrogen 11·11.

Purification of the Crude Gutta-percha, and Uses of the Purified Material.—The blocks of crude gutta-percha, in the condition in which they arrive in this country, contain many foreign substances adventitiously and designedly introduced, which it is necessary to eliminate before the material can be applied to any useful commercial purpose. The impurities alluded to are chiefly mechanical, and consist mainly of sand, earthy matter, and fragments of wood, bark, leaves, &c. The exact method of removing these impurities differs somewhat according to the use to which the finished product is to be applied, and it must therefore be understood that the following description is only a general account, which may in practice be slightly varied, as occasion requires.

The first step towards the purification consists either in cutting the crude blocks into slices by a machine not unlike a large chaff-cutter, or in reducing them to coarse powder by a suitable rasping machine. The usual method, however, is that of slicing; and this is accomplished by a machine which was devised by CHARLES HANCOCK and patented by him in 1847. This machine is a large solid vertical disc of iron, armed on one side with sharp knife-

edges, and revolving at the rate of 200 turns per minute against the extremity of a sloping iron table. The block of gutta-percha being brought to the edge of the table, is rapidly caught by the knives and literally reduced to shavings, which fall into a receptacle beneath. Fig. 2 is a side elevation of this machine, and Fig. 3 a front elevation of the disc, with part of the frame. The revolving disc, B, is a circular iron plate, of about 5 feet diameter, into three slots in which are inserted three radial knives, *b*, *b'*, *b''*, in a similar manner to the iron of an ordinary plane or spoke-shave. Supported by the frame, A F, is the shaft, D, to one end of which the plate, B, is attached, and to the other the strap-pulleys, E, by one of which motion is communicated to the shaft from a steam engine of considerable power. F is an inclined shoot, down which the lumps of the crude material are dropped against the knives of the revolving disc, and are thus cut into slices, the thickness of which depends upon the degree of projection given to the knives. In the figure the knives are represented as being straight, but Hancock states in his specification that in cases where the crude material is of an unusually hard or intractable nature, the knives used may be advantageously of a curved or reaping-hook form, in order to make their action more gradual. In the cutting process, the knives often suffer considerable injury from the stones and other intractable substances introduced as adulterants by the Malayan natives.

Fig. 2.

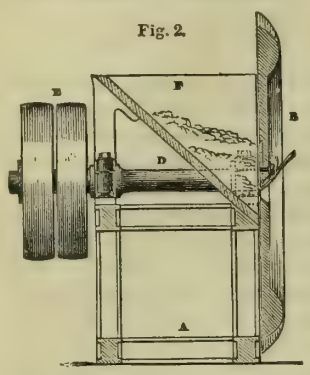
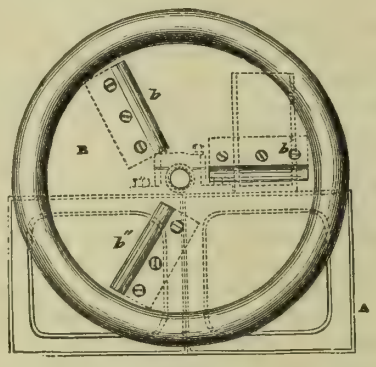


Fig. 3.



Having been reduced to shavings, or rasped to a coarse powder, the next process to which the gutta-percha is subjected is that of cleansing it from a greater part of the extraneous matter which is present. There are two methods of effecting this. In the original patent of C. Hancock, before alluded to, the method of treatment was to subject the slicings of gutta-percha to the action of a series of "tearing" wheels placed over tanks of cold water; the finely divided fragments of raw material then fell into the cold water, where the comparatively pure gutta-percha floated and the earthy impurities which it previously contained fell to the bottom. The floating material was caught by an endless band revolving over two rollers, and by which it was taken to a second tearing wheel; the same operation being in all repeated some three or four times. Finally, the purified gutta-percha was carried between a series of small rollers, and subsequently on its issue from the water it was caught by a pair of larger rollers, from which it emerged as a consolidated sheet. The process most generally followed appears to consist in throwing the shavings or raspings of the raw material into a tank of water, into which the waste steam from the boilers is conducted in order to heat it to the boiling point. This process softens the gutta-percha into a fluid mass, and by the agitation of the boiling the grosser impurities separate and fall to the bottom. The greater part of the foreign matter having been thus eliminated, the partially purified material is collected into one mass and carried to "the teaser." This is a sort of large circular box, containing a cylinder or drum covered with rows of bent jagged teeth, and which revolves at the rate of about 800 turns per minute. The mass of the gum is thus rapidly torn into shreds, which fall into a tank of water placed beneath, where the pure material floats on the surface, and the heavier impurities disengaged by the action of the teaser fall to the bottom. The purified gutta-percha has now a crisp, fresh-looking appearance, and is ready for the next operation; which consists in working and kneading it into a homogeneous mass, in order to secure uniformity of composition and expel the air and water which have been introduced in the preceding operations. For this purpose the material is once more subjected to the operation of boiling, by which it becomes united into a single mass, which is then transferred to the "kneader" or "masticator," which is a strong circular iron box of the required dimensions containing a revolving cylinder, either armed with cogs or pins on its surface or having a deeply corrugated or fluted surface. The cylinder and its containing box are both constructed of cast iron, and are heated by means of steam. (A diagram of this machine will be found in the article India Rubber.) The gutta-percha when introduced is by the heating action of the steam retained in a soft condition, and being carried round by the revolving cylinder is forcibly squeezed against the sides of the box, and by the action of the projecting pins or cogs all air bubbles are expelled, and the whole brought to the state of a perfectly homogeneous mass, without a particle of water in its composition.

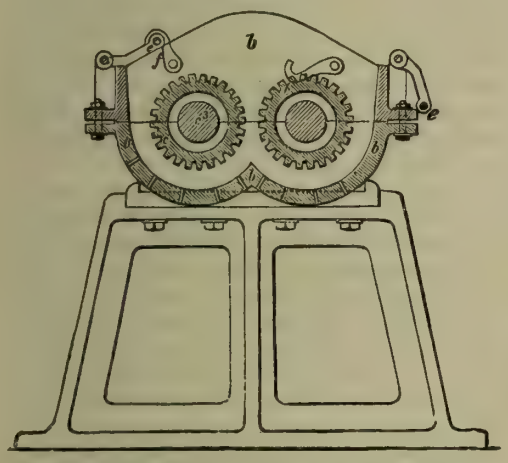
Nickels in 1856 introduced a somewhat different form of masticator, represented in Fig. 4, which is considered very effective in its action. In this machine there are two rollers, with screws on their

surface in place of teeth or projections; the rollers work parallel with a small space between, and the threads of the screw rollers are notched, the notches being made preferably in a diagonal direction.

After being subjected to the masticating process, the gutta-percha is sufficiently pure for being applied to most ordinary purposes. Where, however, it is required of a still higher degree of purity, as, for instance, in its application to covering telegraph wires for submarine cables, or for the manufacture of the fine sheets known as gutta-percha tissue, the material is subjected to a process of straining by being forced in the melted condition through sieves of wire-gauze, hydraulic or steam pressure being used for the purpose. After this straining, a further mastication is practised, in order to expel the last traces of water and render the material perfectly uniform, when, on the completion of the process, the gutta-percha is in its highest state of commercial purity.

The necessity for straining gutta-percha in order to completely purify it may not be at first apparent; but it must be remembered that many of the impurities originally present consist of comparatively light substances (fragments of bark, wood, &c.), which in the ordinary purifying processes float on the surface of the water with the gutta-percha itself, only the heavier foreign substances, such as sand, &c., becoming eliminated by falling to the bottom of the tanks. These lighter impurities are scarcely in any degree eliminated by the various teasing and masticating processes, being only more or less comminuted and mixed to a greater or less degree with the gutta-percha; and it is not until the latter is subjected to the straining process that the complete purification of the material can be said to be effected. At the same time, the impurities alluded to do not in any degree interfere with the more ordinary useful purposes to which gutta-percha is applied, and it is therefore only in comparatively extreme cases that this last stage of purification has to be gone through.

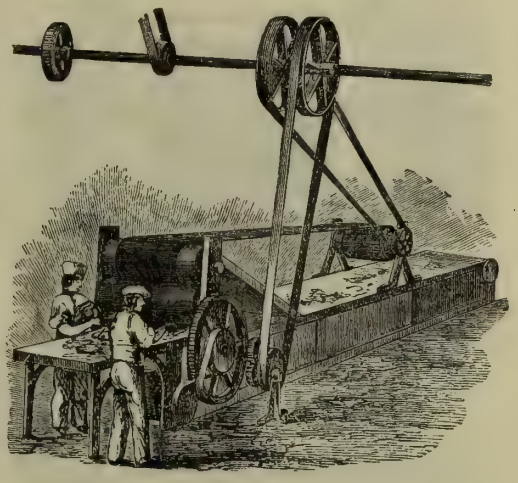
Fig. 4.



Rolling the Purified Gutta-percha into Sheets.—The conversion of the purified material into sheets is the first step necessary for its subsequent manufacture into a great variety of articles of different kinds.

For this purpose, the kneaded mass, fresh from the masticator, and consequently still in a warm plastic condition, is carried to the *rolling machine* represented in Fig. 5. This apparatus is similar to that employed in paper-mills, the gutta-percha, like the soft paper, passing on an endless band between steel cylinders placed at the requisite distances apart, according to the thickness of the sheet required. By means of screws the cylinders can readily be adjusted to produce with equal ease the stoutest driving band, or the thinnest *gutta-percha tissue*, so successfully employed as a substitute for oiled silk, hydropathic bandages, &c. After passing between the rollers in a soft and impressible state, the sheet performs a long journey on the endless band, in the course of which it gradually cools and hardens, and finally appears at the other end a smooth, firm, flat sheet, which admits of being received and wound on a drum till the requisite length has been worked off.

Fig. 5.



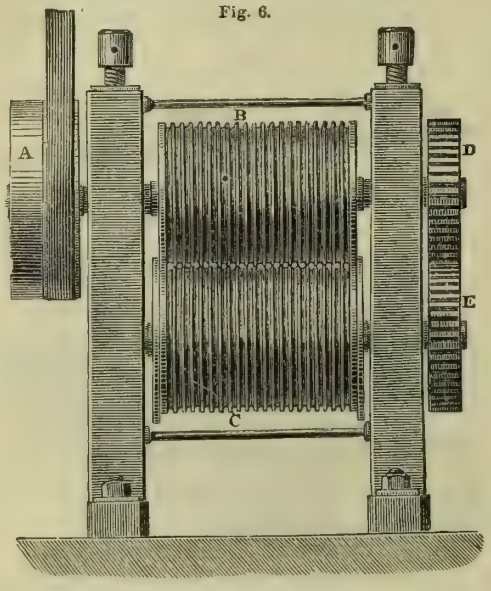
If, however, the sheet be too thick to cool sufficiently by merely travelling the prescribed distance, it is ventilated as it passes along by a series of fans like those of a winnowing machine.

Dividing into Ribands and Cord. — When the material is required to be in bands or strips, it is generally cut into that form, while being rolled into sheets, by a series of knives so placed as to divide the sheet while yet plastic into any number of bands of the required width, just before quitting the rolling machine. The knives are set upright in a frame, edge foremost, at the requisite distances from each other, and without interrupting the progress of the sheet, they slice it into bands, which, as before, are made to travel till they cool, and are then wound upon a drum.

In 1847 an ingenious machine was patented by CHARLES HANCOCK for cutting gutta-percha into narrow ribands, and manufacturing it into thread or cord of any required shape. A front elevation of as much of this machine as is necessary to under-

stand its construction, is given in Fig. 6, in which B C are two grooved rollers, made of steel or iron, and mounted in suitable framework. The grooves of each roller are semicircular, so that when the grooves of one roller are brought opposite to those of the other, they form together a series of circular holes, as shown in the figure, at the line of contact between the two rollers. The under roller is flanged at both ends, and the two ends of the upper roller are made to fit inside of these flanges, in order to keep the cutting edges from shifting or being damaged. From the prime mover, motion is communicated to the wheel, A, on the shaft of the roller B, and thence through the wheels D and E, to the roller C. To cut thin sheets of gutta percha with this machine into narrow strips or ribands, the material is passed through it cold, and only the cutting edges are brought into operation. To make round thread or cord by means of it, a sheet of gutta-

Fig. 6.



percha, of a thickness equal to the diameter of the holes formed by the grooves of the rollers, is passed through it at a temperature of about 200°, by supplying the material from a feeding chamber, heated to that degree by steam or otherwise; and the threads or cords, after passing between the rollers, are received in a tank of cold water, from which they are wound on reels or drums, conveniently placed for the purpose. Or, by another method, the gutta-percha is employed in a plastic state, and passed towards the machine under a gauge, after the manner employed in the caoutchouc manufacture.

Should it be desired to produce cord of a semicircular section, the lower grooved roller is replaced by a plain roller; or should cord of a form neither circular nor semicircular, but square, triangular, hexagonal, or of any other angular form, be required, two cylinders are employed, grooved in such a manner as to produce the desired shape.

Cord and thread are likewise manufactured by means of a stamp, bearing a number of close parallel sharp edges, which are brought down upon a sheet of gutta-percha, so as to cut it nearly through in a series of corresponding parallel lines. The narrow slips are then severally torn off, and polished up by hand for use.

Cutting, Shaping, and Moulding. — Besides the operations above mentioned, the gutta-percha, when formed into sheets, admits of an infinite variety of applications. Softened by boiling water or steam, it may be shaped into any required form by the hand, the knife, the mould, and the press.

In making shoe soles, a dozen of stout bands are placed under the action of a cutter, which divides them into rectangular pieces of the required size, which are afterwards cut, *en masse*, into the required shape by means of a sharp-edged frame. By means of revolving tables, bearing inverted iron moulds of various shapes, all kinds of moulded articles, such as buckets, bowls, bottles, mariners' hats, &c., are made, in much the same way as clay articles are fashioned on a potter's wheel. Many other articles used formerly to be made from gutta-percha, which the increased price of the material now precludes. In any stamping or moulding process the sheets are cut into pieces of the desired size, and each piece then sufficiently warmed to take the impress of the dye; the impressions are wonderfully sharp when properly executed, the most minute details being reproduced with perfect fidelity.

An ingenious method of moulding was patented by Charles Goodyear in 1855. A cylinder or barrel, fitted with a closely-fitting piston, and having screw mechanism by which the piston can be forced slowly and strongly down, is filled with purified gutta-percha. The cylinder is steam-jacketed, so as to keep the material in a plastic condition. At the base of the cylinder is a nozzle or orifice which can be connected at pleasure with any desired mould. The moulds are made in two pieces, held together with bolts or nuts, and having on their interior surface the configuration for producing the article desired, and each mould has two or more entrances suitably situated, the larger of which is used for the entry of the gutta-percha, and the smaller for the exit of the air. The moulding of articles by this method is extremely simple, the mould being simply connected with the outlet of the cylinder containing the gutta-percha, and pressure being applied to the piston by means of the screw arrangement, the plastic and semifluid material is forced into the mould, eventually making its appearance at the air outlets. The pressure is then stopped, the mould cooled, if desired, by immersion in cold water, and the article removed.

Gutta-percha Tubing.—On the introduction of the gutta-percha manufacture, one of the first uses to which the new material was applied was for making tubes for every variety of purpose. The insolubility of the material and its indifference to the action of most chemical reagents were properties which would render it invaluable for a great variety of purposes, but unfortunately the "perishing" of the gutta-

percha has very much prevented its more extensive adoption for the special applications named. The comparatively enduring nature of vulcanized caoutchouc, its greater pliability, elasticity, and its power of resisting moderate temperatures without softening, have led to the extensive employment of this material in the construction of tubing for different purposes in place of gutta-percha.

It will, however, be interesting to here describe the mode adopted in the manufacture of tubing of gutta-percha. For this purpose an apparatus is employed similar in principle to that mentioned when speaking of Goodyear's patent for moulding, and in which masses of the soft purified material fresh from the masticator are placed in a steam-jacketed cylinder provided with a piston. The softened material is forced by the piston through the cylinder, which terminates in a mould, that consists of a solid circular piece of metal set within an iron tube, the annular space between the two regulating the thickness of the tubing. The gutta-percha thus leaves the mould in a tubular shape, and in its soft condition would rapidly collapse unless some precautions were adopted of preserving its shape until it has become cooled and rigid. In order to accomplish this, the tubing on its exit from the mould passes into a trough of water about 50 feet in length, along which it travels, being finally wound on to a drum at the other end. The water by filling the tube is thus made to exert an equal pressure on the interior and exterior surfaces, and to at the same time exert a cooling action by which the form of the tube is rendered permanent. The cylinder which supplies softened material is so constructed as to admit of fresh introductions of gutta-percha without stopping the manufacturing process; a tube of 1000 feet in length has thus been manufactured without a single break.

Coating Telegraph Wires.—At the present time this application is, without doubt, the most important of all the uses to which gutta-percha is applied. Much might be written in the way of speculation on the probable retardation which modern civilization would have suffered but for the introduction of such a substance as gutta-percha; which, by its very high insulating power, its imperviousness to water, and its unchangeable nature under certain conditions, seems the material *par excellence*, and fitted above all others for this special application. It was especially remarkable that the commercial utility of gutta-percha was being recognized almost contemporaneously with the introduction of those magnificent projects by which the earth was, to quote the graphic expression of an eminent writer, "being girdled by wires of living intelligence." Faraday was the first who proposed the employment of gutta-percha for insulating purposes, pointing out that for this purpose it was fully equal to shellac, but that owing to its physical characteristics of toughness and flexibility it possessed many advantages over the more brittle material. It was some time before the conditions necessary for preserving gutta-percha in its unaltered condition were understood, and several failures were due to this cause. Out of a length of 700 miles of covered wire sent some time back to India, about 500 miles had become perfectly useless on its arrival, owing to the covering material having become brittle and resinous—having, in short, perished. This is now obviated by keeping the cables after manufacture in tanks of water, it having been found from experience that under these conditions, and with exclusion of light, gutta-percha is practically unchangeable.

Telegraph wires are coated with gutta-percha by a method exactly the same in principle to that employed in the manufacture of tubing. The machinery now in use at such places as the works of Siemens Brothers is more perfect than that previously used, and of a slightly different description, but the principle is the same.

The central conducting wire of the cable of 1857 was "a strand" made up of seven of the purest copper wires of the gauge known in the trade as No. 22; it was about one-sixteenth of an inch in diameter, and was formed of one straightly drawn wire with six others twisted round it. This strand received a coating of three separate layers of refined gutta-percha, bringing up the total diameter to about three-eighths of an inch. The gutta-percha employed for this work was prepared with the greatest care, the crude material being subjected to repeated raspings, boilings, and tearings, and being finally forced, at the temperature of boiling water, through sieves of wire gauze attached to the bottom of hollow vertical cylinders, and afterwards receiving a final mastication to expel the last traces of water and render the mass perfectly compact and homogeneous. The purified gutta was then introduced into horizontal cylinders, and through these, which were heated by steam to keep the material in a uniformly soft and plastic state, it was squeezed by means of screw pistons worked down slowly and resistlessly by machinery. Under this pressure the gutta-percha emerged, as in tube moulding, through a die, which received the termination of two cylinders and which at the same time had the strand of copper wire moving along through its centre, instead of being stationary like the mandril in tube moulding. The strands were drawn forward between the cylinder and through the die by a revolving drum. They entered the die in the form of bright copper wire, and issued from it like brown cord of gutta percha. Six of these strands were coated together, ranging along side by side; and this operation was repeated a second and third time, to produce what is termed "the core" of the cable.

In the modern methods of coating cables pure gutta-percha, prepared by the greatest care, is employed; and besides this, various insulating compounds are used. The wire before being covered with the pure material is generally run through a compound of Stockholm tar, gutta-percha, and resin, heated until in a sufficiently fluid condition for the purpose. The gutta-percha used for the pure coatings is prepared in the way already named, by being rasped, ticked (the technical term for the process

of tearing into shreds), masticated, and finally strained through wire gauze; the latter operation being sometimes repeated as often as a dozen times, the material being eventually rolled into slabs and stored. These slabs, when reqired for use, are softened in hot water and re-masticated.

The following table will give an idea of the comparative quantities by weight of gutta-percha and metal in coated wires of different gauges and diameters:—

WEIGHTS OF COPPER AND GUTTA-PERCHA. SILVERTOWN TABLE, PER NAUT OF 2029 YARDS.

Gauge.	Diameter.	Copper.	Gutta Percha.
		Lbs.	Lbs.
1	·310	1773·4	192·7
2	·280	1434·7	155·9
3	·260	1246·5	135 4
4	·240	1058·4	115·0
5	·220	893·7	97·0
6	·200	729·1	79·2
7	·187	635·0	69·0
8	·166	493 9	53·6
9	·158	446·8	48·5
10	·137	329·2	35 7
11	·125	282 2	30·6
12	·109	211·6	23·0
13	·095	164·6	17·8
14	·083	117·6	12·7
15	·072	94·0	10·2
16	·065	70·5	7·6
17	·056	47·0	5·1
18	·049	42·3	4·6
19	·042	30·5	3·3
20	·035	21·1	2·3

Vulcanization of Gutta-percha.—This is effected in exactly the same way and with the same materials as in the case of caoutchouc; but as the vulcanization of gutta-percha is in very limited use now, if indeed it is ever practised, the methods of treatment and processes employed will be fully described under the article on India Rubber, to which the reader is referred for further information on this branch of the subject.

Bleaching of Gutta-percha.—The perfectly white material used for teeth stopping, and sold for that purpose in small square pieces, is prepared by a process patented in 1859, and known as Cattell's method. In Cattell's patent the principle by which the decolorization and purification of the crude material is effected is that of dissolving the gutta-percha in its state of ordinary commercial purity in some suitable solvent, and then effecting the separation of the pure gutta, leaving the colouring matters with which it is mixed behind in solution. This is effected in two ways. The first method consists in cooling the solution of the material (preferably in benzol) to a temperature of about 0° C., the freezing point of water, when congelation takes place. The mass is then either subjected to pressure or submitted to centrifugal force; in either case the result is the expulsion of the liquid solution, carrying with it the colouring matters originally present, while the comparatively pure and colourless gutta is left behind as a solid mass. The other method of treating the solution consists in the addition thereto of some liquid soluble in the solvent first used, but which does not dissolve gutta-percha. If the original material is dissolved in turpentine or resin spirit, the addition of pyroxylic spirit, fusel oil, or alcohol will cause the precipitation of the purified gutta. If the latter is not obtained sufficiently free from colour by the first operation, the solution and subsequent congelation or precipitation is repeated until the desired result is arrived at.

Another method by which pure white gutta has been prepared consists in adding 3 parts of ether to a solution of gutta-percha in chloroform, and exposing the whole to a temperature below 15° C. for some time, when the gutta is precipitated as a white powder. If a solution of this is spread on to a sheet of glass, a beautifully white film is found, resembling kid-glove leather, and becoming transparent on the application of heat. These films are stated to have been used for the manufacture of the finest kinds of artificial flowers. In 1853 a patent was taken out by Normandy for the decolorization of gutta-percha by filtering its solution in carbon disulphide through animal charcoal. The liquid thus obtained was proposed by the patentee for the manufacture of thin sheets or of small balloons and similar articles by a somewhat novel method. A sufficient quantity of the solution was poured into a vessel of glass having the desired shape, which was then turned about so as to bring the liquid into contact with every portion of the internal surface; the excess of liquid was then drained off, and the vessel suspended mouth downwards. The vapour of the carbon disulphide being extremely heavy, rapidly made its escape, and the film of gutta-percha became dryer and dryer, eventually shrinking slightly, and thus becoming disconnected from the sides of the vessel, when it could be withdrawn. Thin sheets of the gutta-percha were proposed to be made by pouring the solution in a cylindrical bottle, subsequently extracting the film of material, and after cutting off the top and bottom portions, severing the cylinder longitudinally, when it could be opened out into a sheet. The thickness of the membranes formed depended obviously on the viscidity of the original solution.

Various Compounds of Gutta-percha.—Besides the various patents which have been taken out from time to time for the vulcanization of gutta-percha and caoutchouc (a list of the more important of which will be found at the end of the article India Rubber), there have been a large number of patents for mixtures of gutta-percha, of caoutchouc, or of mixtures of the two with various mineral and vegetable substances, either with a view of extending the utility of the materials or of cheapening the production of the manufactured articles.

As an example of these various patents, which are exceedingly numerous, we give a short description of the four following:—T. Forster, October, 1847; A. Lorimer, July, 1848; P. A. Godefroy, June, 1855; and C. Goodyear, August, 1856. In the first of these patents, that of Forster, he claims the

mixing of gutta-percha with animal charcoal, bone charcoal, ground whalebone, "hydrate of sulphur," ground bones, horns, hoofs, &c. The mixture was subsequently scented with fragrant essential oils, musk, tonquin beans, orris root, or gum benzoin, and the compound applied to the manufacture of all sorts of ornamental articles. LORIMER'S patent consisted in the admixture of gutta-percha (or caoutchouc) with burned clay, burned flint, broken articles of porcelain or earthenware, marble, Portland, Cornish, or other stones, all crushed and sifted, also with the oxides of zinc and copper, and the hydrate and oxalate of lime. The mixture, after manufacture, was applied to a variety of purposes, of which one of the principal was the soles for boots and shoes, for which purpose as much as possible of the foreign ingredients were introduced. GODEFROY'S patent consisted in mixing finely-ground cocoa-nut shells with gutta-percha, by which many advantages were presumed to be secured. Lastly, the patent of GOODYEAR was for the combination of gutta-percha with asphalt or pitch, the two substances being united by being melted and stirred under boiling water. The compound thus produced could be vulcanized in the ordinary way, with or without the previous introduction of caoutchouc. In November, 1854, a patent was granted to HENRI JULES DUVIVIER and HENRI CHAUDET for a method of treating gutta-percha with the chloride, bromide, iodide, or fluoride of sulphur, or with the corresponding compounds of phosphorus, boron, silicon, and arsenic, or the bi-chlorides of tin or antimony. Of all these the chloride of sulphur was preferred, so that the patent was really similar to that obtained by PARKES (see INDIA RUBBER). The statements, however, made by the patentees with reference to the properties of different mixtures of gutta-percha and chloride of sulphur are interesting.

1. By mixing only 2 per cent. of chloride of sulphur, or only 15 per cent. of the other substances, with the sirupy solution of gutta-percha, a compound is obtained which does not materially differ from gutta-percha in its properties.

2. When more than 2 per cent. of chloride of sulphur is employed, the compound can be extended when heated to 100° or 120° Fahr., and it remains extended when cooled, but retakes its original form when again heated; and at about 212° Fahr. it agglutinates.

3. When 5 per cent. of chloride of sulphur is added, the compound only differs from that just described in being less softened by heat, and in being slightly elastic when cold.

4. When 10 per cent. of chloride of sulphur is added, the properties of the gutta-percha are quite changed, and the compound is unaltered by a temperature of 212° Fahr.

5. When above 15 per cent. of chloride of sulphur is added, the compound becomes horny and harder as the quantity of chloride of sulphur increases.

The most interesting and important patent in connection with the manufacture of gutta-percha is the original patent of HANCOCK (CHARLES), dated 10th August, 1847.

Substitutes for Gutta-percha. — Several patents for the preparation of various substitutes for gutta-percha have been granted at different times; but the so-called "substitutes" have generally been simply mixtures of gutta-percha with resin, pitch, coal-tar, and other substances. Of the *bona fide* substitutes for gutta-percha the gum called "Balata" appears to be in every way the best. This substance is obtained from the milky juice of the *Sapota Mulleri*," or bullet tree, belonging to the natural order *Sapotaceæ*. It grows in Demerara. Some of the gum was submitted by Sir WILLIAM HOLMES to CHARLES HANCOCK, who reported very favourably of it. The *Alstonia scholaris*, growing in Ceylon, is also stated to yield a species of gutta-percha.

Adulterations.—It has been seen, when giving a short epitome of two or three of the patents for compounds of gutta-percha, that a very large quantity of extraneous substances are mixed with the pure material, in order to form compounds for different purposes. It would be scarcely just to term these admixtures adulterations, unless the compounds produced were subsequently intended to be sold under representation of being the pure material, in which case all additions of foreign substances would come strictly under the head of adulterations. The adventitious materials found in the crude gutta-percha are likewise scarcely to be classed *in toto* as adulterations, although there is no doubt that the natives who collect the material are not very particular as to a few stones or fragments of bark, more or less, finding their way into the gutta-percha. There is, however, a genuine adulteration frequently practised by the admixture of gums of an inferior character with the gutta-percha proper. The chief adulterant appears to be the juice of the *Getah Malabeöya*, imported from Palembang, and used for the purpose named by the Chinese. By this admixture various sorts of gutta-percha are obtained differing considerably in price. M. ADRIANI has examined a sample of the "Getah" imported from Palembang. It appeared to be an inspissated milky juice, and was imported in the form of plates of about an inch in thickness, of a greyish colour, somewhat clammy to the touch, and brittle when dried. When cut, it was found a dirty white colour, and contained many impurities. Like gutta-percha, it was dissolved by chloroform. The vessel in which it was contained emitted, on being opened, a disagreeable acid smell. Treated like gutta-percha, and purified by hot water, it was much darker than the raw substance, and often quite black; the smell was equally offensive, and its consistency similar to that of wax or glaziers' putty. The gutta-percha adulterated with the getah was of a loose texture, of a more greyish colour, and of a smell different from that of genuine gutta. In warm water the getah became soft and sticky; treated with boiling water, it formed a neutral milky liquid, which was precipitated by alcohol. When boiled with alcohol it became glutinous, the alcohol extracting a white fat, resembling wax and resin; ether extracted also resin. Being dissolved in chlo-

roform and filtered, a black colouring substance remained behind, which could not be dissolved by the usual solvents, and was burnt without leaving a residue. It appeared to be nothing else but soot. The getah melts at 170° Fahr., and becomes decomposed only at a much higher temperature, when dark-coloured oils are distilled off.

Statistics.—The following table shows the quantities of gutta-percha imported into this country in 1871 and 1872, with the countries from which it came.

	Quantities.	Value, 1871.	Quantities.	Value, 1872.
	Cwts.	£	Cwts.	£
From Holland,	1,498	10,749	5,202	51,432
" France,	346	3,377	621	5,416
" Egypt,	778	6,601	9,814	59,745
" Madagascar,	482	4,700		
" British India, }			2,892	31,000
" Bengal & Burmah, }				
" China,	1,068	11,031	1,660	18,951
" Straits Settlements,	21,227	153,999	23,487	225,789
" Other countries,	812	8,880	921	7,622
Total,	26,211	199,337	45,597	399,955

The price of gutta-percha in 1854 was £4 5*s.* 2*d.* per ton; in 1862 it had risen to £10 12*s.* 8*d.* The present price (1877) charged for the pure manufactured article by the Gutta-percha Company is about 6*s.* per lb.

HEAT.—There are two theories of heat, the *material* theory and the *dynamical*, or mechanical theory. For a long time the material theory had the greater number of adherents. Within certain limits it involved conceptions of a very simple kind, and this simplicity secured its general acceptance. The material theory supposes heat to be a kind of matter—a subtle fluid stored up in the interatomic spaces of bodies. The dynamical theory, or as it is sometimes called, the mechanical theory of heat, discards the idea of materiality as applied to heat. The supporters of this theory do not believe heat to be matter, but an accident or condition of matter; namely, a *motion of its ultimate particles.* Bacon held a view of this kind, and Locke stated a similar view with singular felicity. "Heat," he says, "is a very brisk agitation of the insensible parts of the object, which produces in us that sensation from whence we denominate the object hot; so that what in our sensation is heat, in the object is nothing but motion."

The first to raise the idea of the equivalence between heat and mechanical energy, and of the mutual convertibility of natural powers generally, was Dr. Mayer of Heilbronn in Germany. But to Dr. Joule of Manchester belongs the honour of being the first to give a decisive demonstration of the dynamical theory. His experiments extended from 1843 to 1849; and the result of them was, that however temperatures might differ in consequence of the different capacities for heat of the substances employed, the *absolute* amount of heat generated by the same expenditure of power was in all cases the same.

In this way he proved that the quantity of heat necessary to raise 1 lb. of water 1° Fahr. in temperature is equal to that generated by 772 lbs. falling 1 foot, conversely the heat would raise 772 lbs. 1 foot. Hence the term foot-pound has been introduced, and the quantity of heat necessary to raise the temperature of a pound of water 1° Fahr. being taken as a standard, 772 foot-pounds constitute what is called the *mechanical equivalent of heat.* If the degrees be centigrade, 1390 foot-pounds constitute the equivalent. (Tyndall, "Heat as a Mode of Motion.")

Heats of Combination.—In all chemical changes, when the atoms or molecules are drawn together by their affinities, a certain amount of moving power is developed, which takes the form of heat; and when they are separated again under the action of some superior force, an equal amount of force is expended, and heat disappears. As every chemical reaction consists in such combinations and decompositions, the determination of the thermal effect becomes a complex problem in the mechanical theory of heat. The amount of heat set free, or absorbed, bears always a definite relation to the amount of mechanical or chemical energy, and thus affords a measure of the forces in action. The general principle on which the results of chemical combustion are based appears to be, that whenever a system of bodies undergoes chemical or physical changes and alters its condition, the quantity of heat evolved depends on the initial and final states, and is not affected by the nature or succession of the various intermediate changes, provided, of course, no external mechanical effects have been produced.

Heat is evolved in the combination of certain ponderable substances, as when oxygen and chlorine combine with the metals or other combustible bodies; or when bromine, iodine, sulphur, and phosphorus combine with certain of the metals; or in the combination of acids with bases, or of the stronger acids and bases with water. The amount of heat given out by each element on entering into combination is definite, and bears a specific relation to its combining number. Thus 1 gram. of hydrogen burned in oxygen always give out heat enough to melt 315·2 grams. of ice; 31 grams. of phosphorus burnt to P_2O_5, 1576 grams. of ice; 12 grams. carbon, 700 grams. of ice.

It is rare for chemical combinations to occur without some alteration in the physical condition of the bodies. Molecular changes are nearly always attended with an evolution or an absorption of heat. Change of state from the solid to the liquid, or from the liquid to the gaseous condition, is accompanied by the absorption of a definite amount of heat, while there is evolution of heat when the change is in the inverse direction. The following examples will show the effects of alteration in bulk and physical state. Two volumes of carbonic oxide combine with 1 volume of oxygen to form 2 volumes of carbonic anhydride. The heat emitted is due to chemical action and partly to condensation. On the other hand, absorption of heat will occur when solid carbon combines directly with oxygen to form carbonic

anhydride, and the heat of combustion obtained will be less than that due to the chemical action. To find the heat developed in such a combination it would be necessary to estimate the amount of heat rendered sensible, and to know the total amount of molecular energy in the carbon, in the oxygen, and in the carbonic anhydride formed, as the heat produced by chemical action is equal to the molecular energy of the compound *minus* the molecular energy of both constituents (B. Stewart). But there are no certain means of directly estimating these energies, and we are therefore compelled to combine a certain quantity of carbon in a definite molecular condition and at a definite temperature, with oxygen, also at a definite temperature and pressure, and to ascertain by calorimetry the amount of heat evolved. We shall here refer to two other cases. In the formation of water by the combustion of hydrogen—1st., the two gases unite; 2nd., they condense in the relation of 3 to 2 to constitute vapour of water; 3rd., this vapour passes into the liquid condition. These three actions develop in turn a certain amount of heat, and the heat measured is the sum. Again, when sulphur combines with carbon we may say—1st., that the two solids pass into the gaseous state, which causes an absorption of heat; 2nd., that they combine, which causes an evolution of heat; 3rd., that the sulphide formed returns to the solid condition, thus liberating its latent heat. The thermal units obtained are consequently only the difference between these inverse actions.

The most natural hypothesis, in explanation of these phenomena, is that the total heat disengaged or absorbed during a combination is equal to the algebraic sum of the heats that would be individually disengaged or absorbed by each of the changes which occur during the process, if they were successive and independent. And with respect to the same thermal phenomena of chemical action, the most general result may be held to be that the evolution or absorption of heat in any reaction depends upon the relative stability of the system before and after that reaction (Odling). The passage from a less stable to a more stable arrangement of atoms is always attended with evolution of heat, whether the change be one of combination, as of phosphorus with oxygen, or of decomposition, as in the explosion of nitroglycerin or gun-cotton. This change from a state of unstable chemical equilibrium into a stable chemical equilibrium may be compared to the falling of a weight to the ground when its support is removed. As the one is attended with a certain expenditure of actual motion, so is the other with an expenditure of heat, which is interstitial motion. In attaining chemical equilibrium the elements have formed simple combinations. Just as in raising the weight again a certain amount of force must be expended, so also in separating the elements thus combined, we must exert a direct chemical action, and expend a certain amount of heat or its equivalent of some other force. In their free state the elements possess a potential energy which they lose in combining, and which must be restored to them when they are separated again. For every 2 grams. of hydrogen that unite with 16 grams. of oxygen to form water, there are evolved about 68 thermal units, this unit being the quantity of heat required to raise 1 kilo. of water 1° C. To separate the hydrogen again the same number of units must be restored. Zinc when burnt in the air or in oxygen evolves 86 units of heat for every equivalent (65) in grams. which combines with an equivalent in grams. (16) of oxygen. When dissolved in acidulated water it is oxidized at the expense of the hydrogen, which escapes as gas, the separation of which involves the expenditure of 68 thermal units. The oxidation of 65 grams. of zinc in water is $86 - 68 = 18$, and is therefore only attended with an evolution of 18 thermal units, the remaining 68 constituting the potential energy of the escaping hydrogen.

Heat Evolved during Decomposition, or Chemical Combinations Attended with Absorption of Heat.—In the process of oxidation heat is generally evolved; but it is probable that oxygenated combinations, obtained by indirect methods, may be accompanied by an absorption of heat. Thénard remarked that the decomposition of hydric peroxide is attended with the evolution of heat. Favre and Silbermann state that in this case 1 gram. of oxygen in being set free produces 1303 thermal units. In the combination of the additional atom of oxygen with the molecule of water it is therefore probable that heat is absorbed, 1 gram. of oxygen absorbing 1303 units. The protoxide of nitrogen also, on being decomposed, disengages heat. Dulong found that when carbon, carbonic oxide, or hydrogen is burnt in nitrous oxide, the evolution of heat is greater than when the combination occurs in oxygen. Favre and Silbermann calculated the amount of heat thus evolved in the decomposition of nitrous oxide by burning in it a given weight of carbon. The total heat produced was the sum of that due to the combustion of the carbon, and of that which proceeded from the separation of the constituents of the nitrous oxide. The former being known, the latter could readily be calculated. For each gram. of oxygen set free 1090·5 units are given out. Consequently 1090·5 units should be absorbed in the combination of 1 gram. of oxygen with nitrogen.

In the formation of all the nitrogen oxides there is an absorption of heat, which is greater with the dioxide than the monoxide, and gets gradually less for the remaining three. Their formation being attended by an absorption of heat, their decomposition will necessarily lead to an evolution of heat. These oxides therefore are never formed by direct combination, some external agency being required to cause the gases to unite. Any nitrate accordingly, on account of containing an oxycompound of nitrogen, will evolve heat when it is decomposed; and this partly explains the force possessed by gunpowder and other explosives, where part of the energy is due to the heating of the gases produced. KNO_3 evolves 92,800 units, and $NaNO_3$ 85,600 units on being decomposed.

Evolution of heat also occurs in the decomposi-

tion of the oxides of chlorine, the iodide and chloride of nitrogen, trinitro-glycerin, &c. The elements in these bodies are probably present in some form in which they retain a large share of their heat, ready, however, to be evolved when more intimate chemical union occurs.

We may assume therefore that the reversal of a given chemical action gives rise to a thermal effect equal and opposite to that of the original chemical action, and that the same amount of heat is absorbed in the separation of two bodies as is generated in their combination.

Heat Developed or Absorbed in Change of Physical Structure.—As a general rule, the passage of a solid body from one modification into another is attended with thermal changes, there being usually a development of heat in the transition from the vitreous into the crystalline condition. Soft vitreous sulphur, one of the allotropic forms of sulphur, if heated gradually to 93° C., suddenly rises to 110°, and then assumes the crystalline form. One equivalent of ordinary sulphur, in being transformed into the modification insoluble in CS_2, developes 6204 units; and when vitreous sulphur changes into the same form 7608 units are developed (Favre). The black glassy allotrope of selenium, if heated gradually to 97°, suddenly rises in temperature to 220°, and in this state presents a granular instead of a crystalline fracture. The conversion again of common phosphorus into the red variety is attended by an evolution of heat, 1 equivalent developing 28,246 units (Favre).

In the following brief summary a series of results are given, showing the occurrence of thermal changes in other alterations of structure:—*i.e.* the conversion of prismatic into octohedral sulphur develops (for 1 gram.) 2300 units (Mitscherlich); of insoluble (in CS_2, bisulphide of carbon) sulphur, from flowers of sulphur into octohedral, 2700 units; dissolved octohedral sulphur changing into insoluble sulphur, 12,800 units. On the other hand, there is an absorption of heat when amorphous soluble sulphur becomes octohedral (2600 units for 1 gram.), and when octohedral sulphur dissolves in CS_2 (12,800 units, Berthelot).

Thermal Changes Attending Combustions in Oxygen Gas.—The determination of the heat produced by combustion has occupied the attention of some of the most distinguished chemists, as Lavoisier, Laplace, Rumford, Crawford, Dalton, Davy, Dulong, and Despretz. Prior, however, to the posthumous publication of Dulong's valuable researches, the results obtained were of little scientific value. Lavoisier calculated the heat of combustion from the quantity of ice melted in his calorimeter when given weights of the bodies were burnt in it; but neither his experiments nor those of Laplace on the same subject have any claim to scientific accuracy, although Lavoisier's experiments on the heat of combustion of charcoal are deserving of special reference, as his results with very imperfect apparatus agree closely with those obtained by subsequent observers. By the investigations of Despretz, and more especially of Andrews, our knowledge of the heats of combination has attained its present condition. The names of Grassi, Hess, Abria, Favre, Silbermann, Thomsen, and Berthelot must also be mentioned as having contributed largely to this result.

General Methods Employed in Determining these Thermal Changes.—Rumford made use of a calorimeter, consisting of a thin copper box filled with water, and containing a serpentine tube with both its ends open to the air, through which the heated products of combustion circulated. Despretz perfected this apparatus. He caused the body to burn in a large platinum crucible, which received a constant supply of oxygen gas, the formed products escaping also by a serpentine tube. The whole apparatus was plunged in a calorimeter full of water, which absorbed the heat. About the same time Dulong was engaged on this subject, and his apparatus consisted of a combustion chamber supplied with oxygen, and plunged in a vessel of water. The combustion products passed through a worm, and were collected in a gasometer to be measured and analyzed.

Andrews' experiments, which were performed with unusual accuracy, were made as follows, when the bodies to be combined and the products were gaseous:—The purified gases were first introduced in their combining proportions into a vessel of thin sheet copper, which was so connected with a voltaic battery that, when the circuit was completed, a fine platinum wire in the gas through which the current passed was heated to whiteness, and the mixed gases thus exploded. This copper vessel was placed in one of large capacity, containing a known quantity of water, and this latter was suspended in a cylinder with a movable cover at each end. The whole was finally inclosed in an outer cylindrical vessel, so arranged as to admit of rotation around a horizontal axis. The initial temperature was taken by a very delicate thermometer after the apparatus had been rotated for some time, so as to bring all its parts to a uniform temperature. The gases were then exploded, and the apparatus rotated for thirty-five seconds to establish an equilibrium of temperature. The temperature was now taken, and it was again taken after a further rotation of the apparatus for thirty-five seconds to ascertain the cooling effect of radiation. The calorific capacity of the apparatus being known, the heat of explosion could readily be calculated.

When solid bodies were burned in oxygen the apparatus was somewhat different; but the principle was the same. The combustion was effected in a copper vessel of about 4 litres capacity filled with oxygen; and the body to be burned was placed upon a small platinum dish in the interior. Ignition of the body was effected by a voltaic current, but in some instances minute pieces of phosphorus of known weight were used to kindle the body. This vessel was immersed in a known quantity of water, protected from radiation by a number of surrounding envelopes. When chlorine was used instead of

oxygen the body was inclosed in a thin glass capsule that was broken by agitation when required.

Favre and Silbermann employed a gilt brass vessel for combustions, which was placed in a silvered-copper calorimeter of 2 litres capacity. The latter was protected from radiation by an outer vessel lined with swansdown, which was in turn inclosed in a double envelope filled with water. The dried oxygen was conveyed through a tube into the combustion chamber, and the superfluous oxygen and the products of combustion were made to pass through a copper coil immersed in the water of the calorimeter, so as to be completely cooled to the temperature of the surrounding medium. Solid bodies were kindled by introducing pieces of burning charcoal; liquids were burnt upon asbestos wicks; and gases were introduced through a burning jet. The weight of the substance burned was generally ascertained by weighing the products of combustion.

Hydrogen and Oxygen.—Taking the mean of the numbers obtained by Andrews in his experiments, we deduce for the heat produced during the combination of—

1 litre hydrogen with oxygen,	3036 units.
1 litre oxygen with hydrogen,	6072 "
1 gram. oxygen with hydrogen,	4226 "
1 gram. hydrogen with oxygen,	33,808 "

The unit here employed is the same as that adopted by Dulong, being the amount of heat required to raise 1 gram. of water through 1° C. The mean of Dulong's experiments gave 3107 units for the heat produced by the combustion of 1 litre of hydrogen gas. As the heat obtained in the union of hydrogen and oxygen is partly due to the condensation of the vapour formed, a correction must be applied. Assuming the latent heat of steam at 20° to be 611 units, the heat evolved by the condensation of 1·125 gram. steam will be 687, which, taken from 4226, leaves 3539 for the true heat due to the chemical combination of 1 gram. oxygen with hydrogen (Andrews). The following numbers may be added to those given in the table, as indicating the number of grammes of water raised 1° C. by the combustion of 1 gram. of oxygen with hydrogen—2578 (Despretz), 2672 (Lavoisier), 3000 (Dalton), 4349 (Hess), 4500 (Crawford), 4333 (Grassi).

Kiechl has measured the heat generated during the combustion of hydrogen, or its equivalent, the quantity absorbed when 1 gram. of hydrogen is produced by the decomposition of water, by comparing the heat evolved by an electric current in a voltameter, during the decomposition of a known weight of water, with that generated at the same time by the same current in passing through a wire whose resistance is equal to that of the voltameter. He gives it as 33,653 units. Thomsen assigns the number of units as 34,034.

Of all substances, hydrogen possesses by far the greatest heat of combustion. This accounts for the intense heating effects which can be obtained with the oxyhydrogen blow-pipe.

Carbon and Oxygen.—The heat evolved during the combustion of 1 gram. of carbon amounts to 7678 units. Correcting for the carbonic oxide formed, 7900 may be taken as representing the quantity of heat disengaged during the conversion into CO_2 (Andrews). Dulong gives 7288, Grassi 7714, and Lavoisier 7237 units.

Influence of Dimorphism.—According to Favre and Silbermann, the development of heat is considerably affected by the physical state of the carbon, as is seen from the following table:—

	Density.	Specific Heat.	Heat Units.
Diamond,	3·55	·147	7770
Graphite,	2·2	·201	7796
Wood charcoal,	·3	·241	8080

The same thing is seen in the case of sulphur and phosphorus.

	Density.	Specific Heat.	Heat Units.
Octohedral sulphur,	2·05	·177	2220
Prismatic "	1·98	·184	2264
Viscous "	—	—	2258
Red phosphorus,	2·1	·170	5070
Vitreous, "	—	·188	5953

Carbon may be supposed to exist in a negative or passive condition, requiring the expenditure of a certain force to bring it into a chemically active state before combination occurs.

As a further illustration of the influence of the physical condition, it may be stated that when the product of combustion is a solid, the heat is more than that due to the chemical action—for example, as when phosphorus is oxidized to P_2O_5. A difference between the specific heat of the compound and of its constituents may also occasion an elevation or depression of temperature.

Equal weights of the same substances, therefore, when in different allotropic conditions, evolve different amounts of heat during combustion; the modification possessing the least density and the highest specific heat evolving the most heat on combustion (Favre and Silbermann).

Another difficulty in the case of carbon is due to the production of a little carbonic oxide in the combustion. Consequently it is necessary to add to the heat collected by the calorimeter what would be obtained by burning the carbonic oxide that is formed.

Carbonic Oxide and Oxygen.—One litre carbonic oxide evolves in its combustion 3057 thermal units; 1 litre oxygen with carbonic oxide, 6114; 1 gram. oxygen with carbonic oxide, 4255; and 1 gram. carbonic oxide with oxygen, 2431 units (Andrews).

As 28 parts by weight of the gas contain only 12 parts by weight of carbon, 1 part of carbon or carbonic oxide must therefore evolve 5607 thermal units on taking up the additional oxygen to form carbonic acid. Deducting this from 7900 (7900 — 5607 = 2293), the difference (2293) indicates the amount of heat evolved by 1 part by weight of carbon in burning to form carbonic oxide. Accordingly, in a furnace in which carbonic oxide is one of the products of combustion there is great waste of energy; for, as the above calculation shows, fuel in burning to carbonic oxide gives out less than one-third of its total heat of combustion (Andrews).

Oxygen with Solid or Fluid Bodies.—Iron, tin, protoxide of tin, antimony, and phosphorus, in their

ordinary physical states, evolve nearly the same amount of heat as carbonic oxide, hydrogen, and cyanogen, in combining with an equal volume of oxygen. But the agreement disappears in great part if we apply corrections for the heat due to the changes of physical state which occur in some of the reactions. Carbon stands about midway between these and the following class of bodies:—sulphur, copper, and the protoxide of copper, which disengage in their combination a little more than half that evolved by the first class. A much larger amount of heat is evolved by zinc, and a still larger quantity by potassium.

In the reduction of oxide of iron by hydrogen no perceptible evolution of heat occurs, while in a similar reduction of oxide of copper there is ignition. The explanation is simple. Hydrogen gas, in combining with oxygen, gives out nearly the same quantity of heat as iron; the separation of the iron from the oxygen accordingly expends as much heat as is evolved by the combination of the hydrogen and oxygen. On the other hand, the heat of combination of oxygen and hydrogen is twice as great as that of oxygen and copper.

Combustion of Compounds.—In general the heat disengaged by the combustion of a compound is less than that emitted by the combustion of its constituents if they were free. In fact, at the moment of their combination the constituent elements have disengaged $\pm$ C heat, which they recover again on becoming free immediately before combustion; they then burn and disengage the same number of units, K, as if they were burnt separately. The heat of combustion of the compound will therefore be K — ($\pm$ C), and will be greater or less than that of its elements according as ($\pm$ C) is negative or positive. Take olefiant gas and alcohol as examples.

	Heat of Combustion. Of Compound.	Of its Elements separately.		Difference.
Olefiant gas,...	11857·8	11848·8	+	9·0
Alcohol,.....	7183·6	7212·3	—	28·7

In organic chemistry there are compounds (hydrocarbons and compound ethers) which have a similar percentage composition, but differ in the number of atoms contained in their molecules—that is, they are formed by the same elements united in equal proportions but differently condensed. Now, among these so-called *polymeric* compounds the greater their condensation the greater was the amount of heat they disengaged in being formed, and the less accordingly ought they to produce by their combustion. This is demonstrated in the following table (Favre and Silbermann):—

ISOMERIC COMPOUNDS.

	Heat Units.
Olefiant gas, $(CH_2)_2$,.....	11,858
Amylene, $(CH_2)_5$,.....	11,498
Paramylene, $(CH_2)_{10}$,.....	11,303
Cetene, $(CH_2)_{16}$,.....	11,055
Metamylene, $(CH_2)_{20}$,.....	10,928

The above bodies differ in composition by a multiple of CH_2, and are called *homologous*. With each addition of CH_2 the heat developed by the combustion of *each gram.* of substance diminishes; but as Berthelot has pointed out, the heat disengaged by the *molecule* for each addition of CH_2 augments by about 155 thermal units.

Certain simple bodies can exist under different physical conditions. Sulphur and phosphorus are examples. When they pass from the ordinary state to the allotropic they absorb heat, and in returning to their ordinary condition they disengage this. There exist also compound bodies having the same elements, and containing the same number of atoms in their molecules, but differently arranged; that is, their chemical composition is identical, and there is the same degree of condensation of their elements, but their properties are different. Their heats of combustion are also different; so we must conclude that their elements in combining had disengaged or absorbed unequal quantities of heat. The difference then between two isomeric bodies as to their thermal heat is as absolute as it is between a simple body in its allotropic forms.

METAMERIC BODIES.

	Empiric Formula.	Thermal Units.
Acetic acid, $H,C_2H_3O_2$,.....	$C_2H_4O_2$	3505
Methylene formiate, CH_3,CHO_2,..	....	4197
Propionic acid, $H,C_3H_5O_2$,.....	$C_3H_6O_2$	4670
Formic ether, C_2H_5,CHO_2,.....	....	5279
Methyl acetate, $CH_3,C_2H_3O_2$,....	....	5344
Butyric acid, $H,C_4H_7O_2$,.....	$C_4H_8O_2$	5647
Acetic ether, C_2H_5, $C_2H_3O_2$,....	....	6293

Frankland has determined the heat of combustion of various articles of food by burning them under water with potassium chlorate, and subtracting the heat due to the decomposition of the chlorate from the total obtained.

If a few grains of ferric oxide be dropped into an ounce or two of fused potassic chlorate which is slowly disengaging oxygen, the evolution of gas immediately proceeds with great violence, and the mixture becomes red hot, although the external application of heat be discontinued. The ferric oxide remains unaltered. It is thus obvious that potassic chlorate in being decomposed furnishes more heat than that which is necessary to gasify the oxygen which it evolves. The amount of heat thus evolved by the quantity of potassic chlorate (9·75 grams.), mixed with 1 gram. of the substance burnt in each of the following determinations, was effected by the use of two copper tubes, the one placed within the other. The interior tube was charged with a known weight of potassic chlorate and ferric oxide, whilst the space between the tubes was filled with a mixture of chlorate and spermaceti, whose calorific value was known. The heat generated during the combustion of the latter mixture in a calorimeter effected the complete decomposition of the chlorate in the interior cylinder.

HEAT DISENGAGED BY 1 GRAM.

Muscle of beef,.....	5103
Purified albumen,.....	4998
Fat of beef.....	9069
Hippuric acid,.....	5383
Uric acid,.....	2614
Urea,.....	2206

HEAT DEVELOPED DURING COMBUSTION IN OXYGEN.

Substance Burned.	Heat units—Grams. of Water raised 1° C. by 1 Gram. of each Substance.	Grams. of Water raised 1° C. by combination of 1 Gram. of O.	Calorific Equivalent. Grams. of Water raised 1° C. for 8 Grams. (1 Eq.) of O.	Compound formed.	Observer.
Hydrogen,	34,462	4307	34,462	H_2O	Favre & Silbermann.
"	33,808	4226	33,808	"	Andrews.
"	34,743	4343	34,743	"	Dulong.
Carbon,	8,080	3030	24,240	CO_2	Favre & Silbermann.
"	7,900	2962	23,096	"	Andrews.
"	7,912	2967	23,736	"	Despretz.
Sulphur,	2,220	2220	17,760	SO_2	Favre & Silbermann.
"	2,307	2307	18,456	"	Andrews.
"	2,601	2601	20,808	"	Dulong.
Phosphorus,	5,747	4509	36,072	P_2O_5	Andrews.
"	5,669	4394	35,148	"	Abria.
Zinc,	1,301	5285	42,282	ZnO	Andrews.
"	1,298	5273	42,185	"	Dulong.
Iron,	1,576	4134	33,072	Fe_3O_4	Andrews.
"	1,702	4340	34,720	"	Dulong.
Cobalt,	1,080	3995	31,960	(?)	"
Nickel,	1,006	3723	29,784	NiO	"
Tin,	1,233	4545	36,360	SnO_2	"
"	1,144	4230	33,519	"	Andrews.
Antimony,	961	5875	47,000	Sb_2O_4	Dulong.
Copper,	602	2394	19,152	CuO	Andrews.
"	632	2512	20,096	"	Dulong.
Carbonic oxide,	2,634	4609	36,876	CO_2	"
"	2,431	4258	34,034	"	Andrews.
"	2,403	4205	33,042	"	Favre & Silbermann.
Stannous oxide,	534	4473	35,784	SnO_2	Dulong.
"	521	4349	34,792	"	Andrews.
Cupreous oxide,	256	2288	18,304	CuO	"
"	244	2185	17,480	"	Dulong.
Cyanogen,	5,195	4221	33,768	—	"
Marsh gas,	13,063	3266	26,128	—	Favre & Silbermann.
"	13,185	3296	26,368	—	Dulong.
"	13,108	3277	26,216	—	Andrews.
Olefiant gas,	11,942	3483	27,864	—	"
"	11,858	3458	27,664	—	Favre & Silbermann.
"	12,030	3514	28,112	—	Dulong.
Alcohol,	6,909	3511	26,488	—	"
"	6,850	3282	26,256	—	Andrews.
"	7,183	3442	27,536	—	Favre & Silbermann.
Ether,	9,027	3480	27,840	—	"
Olive oil,	9,862	—	—	—	Dulong.
Oil of turpentine,	10,852	3294	26,352	—	Favre & Silbermann.
Carbonic disulphide,	3,401	2692	21,536	—	"

Combustion.—The great mass of the atmosphere which surrounds the globe consists of oxygen and nitrogen, mixed in the proportion, by volume, of 20·96 parts of oxygen to 79·04 of nitrogen, and by weight, of 23·185 parts oxygen to 76·815 nitrogen. The air always contains in addition variable quantities of aqueous vapour, carbonic anhydride, and ammonia. Nitrogen is very inert in its properties, and acts simply as a diluent of the more active oxygen. The affinities of oxygen are very great, as it tends to enter into combination with nearly every other elementary substance, and with many compounds not already saturated with oxygen. Under certain conditions wood, coal, petroleum, sulphur, phosphorus, and such bodies will unite with it and give rise to the evolution of light and heat. This process is called combustion, and the bodies with which the oxygen combines are called combustibles. All ordinary cases of combustion consist in this active process of oxidation.

In its usual acceptation the word combustion indicates the combination of a body with the oxygen of the air, a combination that is attended by a disengagement of heat and often of light. But in a more general sense it designates every direct combination that occurs with sufficient energy to give rise to analogous phenomena; as the combustion of copper in vapour of sulphur, or of finely divided antimony in chlorine gas. Besides the cases of combustion where the burning body obtains its oxygen *from without*, it may also occur between the atoms of a mixture or chemical compound, as when gunpowder or nitro-glycerin is exploded; such may be called cases of *internal* combustion.

As types of our ordinary combustibles let us take hydrogen, charcoal, benzol, and alcohol, and study the reactions when these bodies are burnt: α, $2H_2 + O_2 = 2H_2O$; that is, 2 volumes of H gas, and 1 volume of O gas combine to form 2 volumes of aqueous vapour. β, $C + O_2 = CO_2$; carbon with oxygen forms carbonic anhydride. γ, $2C_6H_6 + 15O_2 = 12CO_2 + 6H_2O$; benzol with oxygen yields carbonic anhydride and water. δ, $C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$; alcohol also yields the same compounds as the last when burnt. In the burning of carbon a given volume of oxygen gas yields its own volume of carbonic anhydride.

When a body burns, the molecules of oxygen in the surrounding atmosphere rush upon it with immense velocity, in obedience to the powerful attractive force of affinity. At the moment of

chemical action their motion is suddenly arrested, and their moving power is diffused among the surrounding molecules, showing itself in the phenomena of heat and light. There is here an actual conversion of the force of motion into the forces of heat and light.

The quantity of heat evolved varies with the nature of the combustible. The table below gives the calorific power—that is, the heat evolved by 1 kilog. burnt in oxygen gas—of a number of ordinary combustibles:—

(FAVRE AND SILBERMANN).

Hydrogen,	34,462
Marsh gas,	13,063
Olefiant gas,	11,858
Ether,	9,027
Alcohol,	7,184
Sulphur,	2,221
Wood charcoal,	8,080
Carbonic oxide,	2,400
Dry wood, (about)	3,654
Bituminous coal,	7,500

When the composition of a fuel is known, its calorific power may be calculated approximately. A pure hydrocarbon, like benzol, contains no oxygen, but this element is present in most ordinary fuels. The heat of perfect combustion of one of these fuels is equal to that which would be given out by the combustion of all the carbon, and of so much of the hydrogen as is in excess of that required to combine with the oxygen that is present to form water. To get the available heat we must deduct the amount of heat required to convert into steam—1st., the water formed by this union of the oxygen present with the hydrogen; 2nd., that formed by the combination of the atmospheric oxygen with the rest of the hydrogen in the body; and 3rd., any hygroscopic water that may be there. Suppose we calculate the calorific power of air-dried wood, whose composition is C = 400, H = 48, O = 328, N and ash = 24, hygroscopic water = 200. We then find:—

Quantity of H in combination with O,	41
" available as fuel,	7
" H_2O formed by burning 48 parts H,	432
Hygroscopic water,	200
Total quantity of water evaporated,	632

	Units of Heat.
400 grams. C yield,	3,232
7 " H "	241
	3,473
Deduct amount of heat required to convert 632 grams. H_2O into vapour,	339
Calorific power of air-dried wood =	3,134

(COOKE).

Heat is supposed to be due to the motion of the molecules of bodies, and the greater the moving power of the molecules the higher the temperature. Whatever may be their size or weight, we assume that they must all have at the same temperature the same moving power. But as the molecule of hydrogen is so much lighter than that, say, of carbonic anhydride, it must move much faster to produce the same effect. Let m be the mass of the molecule, and V its velocity at any given temperature; then the moving power will be $= \frac{1}{2}mV^2$. With the increase in temperature there is an increase in the moving power of all the molecules, and the sum of all these moving powers represents the amount of heat the body contains—that is, $S\frac{1}{2}mV^2$. But to measure quantity of heat, an arbitrary standard, the thermal unit, in other words, the amount of heat required to raise the temperature of a kilogram. of pure water from 0° to 1° C., is employed, and this unit represents an amount of moving power that can raise 423 kilograms. through one métre. The burning of a kilogram. of charcoal produces an amount of heat equivalent to 7900 × 423 = 3,346,700 kilogrammétres of work. The steam-engine is a machine for converting this energy of heat into the energy of motion, but even in the best engines not much more than one-twentieth the energy of the fuel is utilized. One of the great problems of the age is to find an engine that will effect this transformation with the greatest economy of power.

To cause a combustible body to burn, it must be heated to a particular temperature, and maintained at that temperature. Increased temperature merely meaning an increased velocity of molecular motion, a requisite molecular momentum must be attained to bring the atoms of O near enough to unite with the combustible. This, the so-called point of ignition, is tolerably constant for each substance, but varies greatly with different bodies, some kindling below the boiling point of water, and others requiring a white heat. To continue burning, the body must be maintained at the temperature of ignition, for if cooled below this it goes out. When the process is once started the heat developed by the chemical union is sufficient to maintain the temperature of the adjacent mass at the ignition point.

To effect the complete ignition of a body, and thus obtain its maximum effect, a definite amount of air is required. Let us calculate the weight needed to burn, say, a kilogram. of coal. By the formula CO_2 it is seen that 12 parts by weight of carbon require 32 parts by weight of oxygen, that is, $2\frac{2}{3}$ times its weight of oxygen. Air contains 23 parts per cent. by weight of oxygen, therefore 23 : 100 :: $2\frac{2}{3}$: 11·56; whence 11·56 kilograms. of air are needed. Coals usually contain some unburnt hydrogen, so more oxygen than this is necessary. Accordingly, we must allow at least 12 kilos.; 1 cubic métre of air at 15° C. weighs 1·293 kilos.; therefore 12 kilos of air will occupy about $9\frac{3}{4}$ cubic métres, so 1 kilo. of coal needs about $9\frac{3}{4}$ cubic métres of air to burn it completely.

The *calorific intensity* of fuel must be distinguished from its *calorific power*. The total quantity of heat developed by the combustion of a body is its calorific power, and is not materially influenced by the rapidity of the process; if the combination is slow the heat may be dissipated rapidly, and a high temperature not attained. Now by calorific intensity is meant the maximum temperature developed, and the temperature of a burning fuel will mainly depend on the rapidity with which the heat is developed as compared with the rapidity of its dissipation. The calorific intensity can be calculated from the calorific power and the specific heats of the products of combustion. Let c = calorific power: w, w', w'',

&c., = weights of combustion products: and s, s', s'', &c., their specific heats. Then—

$$T = \frac{c}{ws + w's' + w''s''}$$

The calorific intensity of all combustibles is much less when burnt in the atmosphere than in oxygen, that is, it is reduced by the presence of nitrogen, and the active energies of oxygen are kept within certain limits. Briefly it may be stated, that the quantity of heat evolved by the same chemical action, whether rapid or slow, is invariable; that the temperature or intensity of heat is variable, being dependent upon the rapidity of the action, and upon the amount and kind of matter heated; and that there is correlative increase in rapidity of action with increase of temperature. When the action is very slow the heat is dissipated as fast as it is generated, and no light and comparatively slight elevation of temperature is produced: this slow combustion is termed eremacausis, of which a good example is seen in the production of animal heat. The processes of combustion differ from other examples of synthesis chiefly in the union of the atoms being attended with an extraordinary development of energy. The intensity of the effect we have seen depends on the rapidity of the combustion, the energy manifesting itself as heat, and also as light, when non-volatile solid particles are present.

Reference may here be made to the *influence of dilution and pressure on the inflammability of gaseous mixtures.* Considerable dilution of an inflammable mixture with one of its constituents may hinder completely its explosion. One volume hydrogen gas mixed with 2 to 9 volumes oxygen will combine and give rise to the same amount of condensation; but above this limit the condensation diminishes rapidly until we arrive at 16 volumes oxygen, when it ceases entirely. The same thing happens if we add the hydrogen in excess. The fire-damp (CH_4) is exploded by the contact of a flame when it is present in the proportion of 6 to 8 per cent. in the air of mines. The explosion becomes still more powerful when it forms 15 per cent. of the air; but when it rises to 25 per cent. explosion will no longer occur.

Under the pressure of several atmospheres candles burn with brighter flame, and it is possible to lower the temperature of ignition by compressing the gas in which a body is burning. The inflammability of most detonating mixtures by the electric spark decreases with the pressure: thus, a detonating mixture reduced to one-eighteenth of its ordinary density will not explode if a spark be passed through it. A jet of hydrogen will burn in air one-fourth its usual density, but will be extinguished if the density be still further reduced to one-sixth or one-eighth. And so with other bodies; but there is considerable difference among them in this respect, for sulphur will continue to burn if the air be rarefied fifteen times, and phosphorus, if it be reduced to sixty times its normal density. Some of the so-called catalytic actions may be explained by supposing that on the extended surface of such bodies as spongy platinum, which manifest a catalytic action, oxygen gas is strongly compressed, if not liquefied, and that the reactions are effected under this pressure.

High temperatures, as we have seen, appear to favour chemical actions, while low temperatures retard them. Oxygen and hydrogen are without action on each other in the cold; liquefied ammonia at —65° C. will not unite with strong sulphuric acid; and iodine and phosphorus will not combine below freezing point.

Theory of Combustion.—The theory of combustion, known as the phlogiston theory, was first advanced in 1682 by Becher, and was afterwards elaborated by Stahl. The principle of fire, according to this theory, is everywhere diffused, but enters unequally into the composition of bodies, combustible bodies being rich in phlogiston, and losing it when they are burned. That this theory is not absurd is seen from the fact that it contained the germs of the modern doctrine of conservation of energy. A combustible body does actually lose something in burning: phlogistic chemists called it phlogiston, modern chemists call it *energy.* It loses the power of emitting a certain quantity of heat—that is, a certain amount of potential energy. Stahl clearly saw that the chief characteristic of burning was the development of energy, though he did not comprehend its real essence; but he recognized it as a fundamental principle of nature. The chemical change occurring in the process was discovered by Lavoisier. He ignored, however, the more important phenomenon, and was wrong in attributing to oxygen alone, and to its reduction of volume, the heat disengaged in combustion. Davy and Berzelius attributed the heat and light evolved in combustion to the combination of the opposite electricities supposed to reside in the atoms of the combining bodies. The combination of the atoms is now regarded as due to the force of affinity. The metal and the oxygen before combining are endowed with a certain quantity of energy, which they partly lose as heat in their union. As in a raised weight there is a certain amount of energy of position equal to the force expended in raising it, so in free carbon or free oxygen there is also a definite amount of potential energy stored up, ready to be given out under favourable conditions. In carbonic acid these elements are united by chemical affinity. To rend them asunder an expenditure of some other force is required. In a leaf, under the agency and at the expense of the sun's rays, this forcing asunder is accomplished; and it is the energy of these rays which is transformed into the potential energy, or energy of position, represented by the chemical separation of the oxygen and carbon. The free carbon and oxygen then become forms of potential energy, and when they recombine this energy will be given out again in the form of heat.

To recapitulate: Stahl believed heat to be due to the emission of phlogiston; Lavoisier, to the liberation of the caloric combined with the gas; Berzelius, to a neutralization of electric fluids; modern chemists, to a transformation of energy—chemical energy changed into its equivalent of heat.

The several theories may be represented thus:—

Stahl's: Metallic oxide and phlogiston (metal) = metallic oxide + heat.

Lavoisier's: Metal + oxygen and caloric (oxygen gas) = metallic oxide + free caloric.

Theory of Energy: (metal and m energy) + (oxygen and n energy) = (oxygen and p energy) + ($m + n - p$ external energy.)

The theory of combustion is but an application of the principle of conservation of energy to chemical energy, the general equations being the following:—

Elements combining and possessed of m chemical or physical energy = the reaction products possessing $m \pm n$ chemical or physical energy $\mp n$ external energy in any form whatever.

Combustions in Chlorine Gas.—Almost the only direct experiments that have been made on this subject are those of Andrews. Abria, however, made a series of experiments on the combustion of hydrogen and phosphorus in chlorine. Favre and Silbermann's numbers have been deduced from reactions in the humid way, and not by burning the metals in chlorine.

The experimental difficulties, especially in the case of the combination of potassium with chlorine, are very great; but by employing a brass instead of a glass vessel to contain the chlorine, Andrews succeeded in obtaining accurate results. By inspecting the table given below, it will be seen that the quantities of heat evolved during the combination of different metals with chlorine are very different, varying from 13,008 to 3114 units for each equivalent of chlorine. But by comparing them with the numbers given in the preceding table, a general resemblance will be noticed between the amounts of heat obtained during the combustion of the same metal in oxygen and in chlorine. This particularly applies to iron, tin, and antimony. In the case of zinc there is less agreement (6309 with Cl, 5366 with O); and copper gives out nearly twice as much heat with chlorine as with oxygen; while phosphorus gives less heat with chlorine than with oxygen.

Comparing the heat disengaged when the bodies combine with the same volume of chlorine, it will be found that potassium disengages twice as much heat as zinc, and nearly four times as much as tin, antimony, or copper. Andrews obtained, by causing the same bodies to react upon one another in the moist way, results agreeing very closely with those obtained by direct combustion.

Thomsen gives as the heat of combustion of H in Cl 22,000 thermal units, Abria's number being 24,087.

Combination of Cyanogen with Chlorine, &c.—The combination of cyanogen with chlorine yields a large quantity of heat, less or none with bromine, while with iodine there is always an absorption of heat.

Combinations of Bromine and Iodine.—The heat disengaged by the same body in combination with chlorine is greater than that with bromine, and still greater than that with iodine. The calorimetric order is also the same as that of affinity. The greater evolution of heat in the case of chlorine is partly due to its being in a gaseous state before combination. Favre and Silbermann have compared these bodies in analogous conditions, and by dissolving them in enough water, so that there is no evolution of heat when more is added, have experimented with the solution so formed in their mercurial calorimeter. The numbers they thus obtain lead them to believe that the quantities of heat disengaged by each metal in uniting with the same metalloid differ by a constant quantity for each metal quite independent of the metalloid; for example, an atom of iodine in uniting with different metals will disengage the same constant quantity of heat less than an atom of chlorine or a half atom of oxygen in uniting with the same metals. Suppose we arrange the metalloids in one group, and the metals in another in the same line, and take Cl as the starting point. Let Br be at a distance from this equal to 11·6, O at 20·8, I at 24·9, Cu at 34·5, H at 40·1, K at 97, &c. The distance between any two points in the two groups will then indicate the amount of heat disengaged when the metal at the one point combines with the metalloid at the other.

HEAT EVOLVED BY COMBINATION WITH CHLORINE.

Elements.	Grams. of H O raised 1° C. by combination of 1 Gram. of Substance.	Grams. of Water raised 1° C. by combination of 1 Gram. Chlorine.	Grams. of Water raised 1° C. by combination of 1 Eq. (35·5 Grams. Cl).	Compound.	Observer.
Hydrogen,	24,087	678	24,087	HCl	Abria.
"	23,783	670	23,783	"	Favre & Silbermann.
Phosphorus,	3,422 (?)	607	21,548	PCl_5 (?)	Andrews.
Potassium,	2,655	2943	104,476	KCl	"
Zinc,	1,529	1427	50,658	$ZnCl_2$	"
Iron,	1,745	921	32,695	Fe_2Cl_6	"
Tin,	1,079	897	31,722	$SnCl_4$	"
Antimony,	707	860	30,401	$SbCl_3$	"
Arsenicum,	994	704	24,992	$AsCl_3$	"
Copper,	961	859	30,494	$CuCl_2$	"
Mercury,	(?)	822	29,181	(?)	"
Bromine.					
Zinc,	1,269	508	40,640	$ZnBr_2$	Andrews.
Iron,	1,277	298	23,833	Fe_2Br_6	"
Iodine.					
Zinc,	819	209	26,617	ZnI_2	Andrews.
Iron,	463	63	8,046	Fe_2I_6	"

Indirect Methods of Estimating Calorific Equivalents.—On the assumption that the calorimetric effect of a given chemical change can be calculated if we know the effects of all the other changes that occur simultaneously, Dr. Woods suggested that the quantity of heat evolved in reactions might be ascertained indirectly, and that thus the difficulties experienced in effecting direct and complete combustions of the metals in O, Cl, Br, I, or S might be avoided.

This indirect method, which is only an application of the principle of the conservation of energy to chemical reactions, has been made use of by Favre and Silbermann, and especially by Berthelot, in determining heat equivalents, many of which it would be impossible to ascertain otherwise.

In the solution of a metal by an acid, or in the precipitation of one metal by another from one of its salts, heat is evolved. Take the solution of zinc in dilute sulphuric acid. Several chemical processes occur, some attended with evolution, and some with absorption of heat. Heat is *evolved*—1st., by the combination of the oxygen and zinc ($Zn + O = ZnO$), let it $= x$; and 2nd., by the solution of the zinc oxide thus formed ($ZnO + 2HO,SO_2 = ZnO_2SO_2 + H_2$) $= a$. On the other hand, heat is *absorbed* by the separation from oxygen of an amount of hydrogen equivalent to the zinc dissolved; $= b$. a and b are known from previous experiments. Let T be the number of thermal units indicated by the calorimeter. Then $x = T - a + b$. In the solution of 1 gram. of zinc T = 567·9 thermal units; a = 335·54 units; and b = 1060·39 units $\left(= \frac{34{,}462 = \text{calor. eq. of H}}{32{\cdot}5 = \text{Chem. eq. of Zn}}\right)$ Therefore $x = 567{\cdot}9 - 335{\cdot}54 + 1060{\cdot}39 = 1292{\cdot}75$. This approaches very closely to the number obtained by direct experiment, 1301 (Andrews), 1298 (Dulong).

HEAT DISENGAGED BY OXYGEN AND CHLORINE COMBINATIONS, &c., CALCULATED ON THIS INDIRECT METHOD: FOR 1 GRAM. OF SUBSTANCE.

I.—(Favre and Silbermann) 1 Eq. O taken = 8.

	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
H	34,462	23,783	9322	−3606	2741
K	—	2,582	2307	1967	1167
Na	—	4,124	—	—	—
Zn	1,302	1,543	—	—	642
Fe	1,351	1,773	—	—	634
Cu	689	929	—	—	288
Pb	267	432	316	224	92
Ag	56	322	237	172	52

II.—(Thomsen, Berthelot, &c.).

		Units.		Units.
H + Br	=	8.440	$S + O_2 + Aq$	= 78,770
H + I	=	−6.036	$S + O_3 + Aq$	= 142,404
H_2 + S	=	4.512	$NO_2 + O + H,Aq$	= 51,080
N + H_3	=	26.707	CO + O	= 66,810
C + H_4	=	20,414	$N_2O_2 + O_3 + Aq$	= 72,940

Thomsen, from a comparison of the quantities of heat evolved in a large series of chemical reactions, is led to the conclusion that these are all multiples of a common constant of affinity, which is about 18,000 heat units. As $(N_2O_2,O_3,Aq) = 4 \times 18{,}235 = 72{,}940$).

III.—(Ditte).

	For 1 Gram.	For 1 Equivalent.
Mg	6130·5	73,566
Zn	1357·6	44,122
In	1044·6	39,486
Cd	271·1	15,182

Thermal Changes Accompanying Solution.—These have been made the subject of inquiry by Gay-Lussac, Thomsen, Karsten, Chodnew, Graham, Andrews, Favre, Silbermann, and Berthelot. The soluble sulphates, nitrates, and chlorides have been the salts chiefly examined, and the solvents pure water and saline and acid solutions. The results may be thus expressed (Andrews):—

"1. The solution of a crystallized salt in water is always accompanied by an absorption of heat.

"2. If equal weights of the same salt be dissolved in succession in the same liquid, the heat absorbed will be less on each new addition of salt.

"3. The heat absorbed by the solution of a salt in water, holding other salts dissolved, is generally less than that absorbed by its solution in pure water.

"4. The heat absorbed by the solution of a salt in the dilute mineral acids is generally greater than that absorbed by its solution in water."

With anhydrous salts, however, the results are different. If it be one which crystallizes, it will first combine with its ordinary equivalent of water of crystallization. There will therefore be heat arising from the union of the anhydrous salt with water, and heat absorbed by its subsequent solution. In a few cases there is evolution of heat. This is probably due to the preliminary formation of a solid hydrate. Heat is also given out during the deposition of a solid from a super-saturated solution. According to Graham's experiments the sulphates of water, copper, and manganese disengage the same quantity of heat in combining with the first atom of water; and equal quantities are disengaged by the sulphates of magnesia and zinc in their complete hydration. But no simple relation among the different sulphates, &c., has yet been discovered.

For 1 gram. of salt dissolved the following units indicate the amount of heat absorbed (Favre and Silbermann):—

Sulphate of potassium,	35·3
" sodium,	49·1
" zinc,	14·8
Ferrous sulphate,	12·1
Sulphate of aluminium and potassium,	23·1
Chloride of sodium,	8·9
Nitrate of potassium,	70·5
" sodium,	45·5
Phosphate of sodium,	52·3
Carbonate of sodium,	52·7
Oxalic acid,	67·0

With regard to the thermal effects accompanying the dilution of solutions, Marignac finds that the addition of water to the solution of a single salt produces a rise or fall of temperature, which does not exceed 0·2° C. for one-tenth solutions, the one-fourth of this for dilution to one-twentieth, and only the one-sixteenth for dilution to one-fortieth. The mixture of the solutions of two salts, which do not act on each other, generally produces less alteration

of temperature than the simple dilution of these solutions: development of heat takes place where the bases are the same, and absorption where they are capable of forming a double salt. Marignac therefore regards the principle of thermoneutrality—double decomposition of neutral salts without change of temperature—as being incorrect.

Heat Developed in the Combination of Acids with Water.—Hess was the first to attempt to reduce to definite laws the quantities of heat disengaged in the formation of the hydrates of sulphuric acid. The subject has been subsequently investigated by Graham, Abria, and Favre and Silbermann, with somewhat different results.

According to Hess, there exists a simple relation among the numbers which express the quantities of heat set free in the formation of the successive hydrates of sulphuric acid. Designating the heat disengaged in the combination of SO_3H_2O with H_2O by $2a$, the heat set free in the formation of the other hydrates will be—

	Hess.	Abria.	Favre, Silbermann, and Quaillard.
$SO_3 + H_2O$, ...	8a	6a	6a
$SO_3H_2O + H_2O$, ..	2a	2a	2a
$SO_32H_2O + H_2O$,..	a	a	·93a
$SO_33H_2O + H_2O$,..	a	·5a	·53a

$a = 46{\cdot}94$ (Hess); $a = 39{\cdot}33$ (Abria).

The general result of Favre, Silbermann, and Quaillard's experiments is that when 40 molecules of water in grams. are added to 1 molecule of acid, 17,612 heat units are evolved; and that a given quantity of water when added to sulphuric acid evolves the same amount of heat whether it is added at once or by successive additions, there being less heat developed in proportion to the previous excess of water added. Pfaundler's results agree closely with those of the above three observers. Thomsen gives 17,248 units as the heat evolved by adding an excess of water to a molecule of sulphuric acid, and 7560 units as the heat evolved by nitric acid under similar conditions. As with sulphuric acid, the heat evolved diminishes with successive additions of water, but less rapidly at first. Andrews, however, states that a slight fall of temperature occurs when dilute nitric acid is mixed with water. An absorption of heat also takes place when water is added to acetic acid; but when the water exceeds half the weight of the acid a development of heat commences, and continues to increase until more than 5 molecules of water have been added to each molecule of acid. The same thing occurs when alcohol is added to acetic acid.

When a *gas is absorbed by water* there is a considerable evolution of heat. This may be in part due to the latent heat of gaseity given out by the gas in its change of state. Hydrochloric acid gas evolves 449·6, sulphurous acid 120·4, and ammonia 514·3 thermal units for each gram. of gas dissolved in water. When 400 molecules of water are present to each molecule of hydrochloric acid, 17,314 heat units are evolved (Thomsen).

Solution of Metals in Nitric Acid.—When this occurs the oxidation is the principal cause of the heat produced. Other causes of thermal change exist in the combination of the oxide with the acid, in the separation of the elements of a portion of the acid during the solution, and in the condensation of the oxygen gas during the combustion. When the solution occurs in nitro-muriatic acid about one-seventh less heat is produced. One equivalent Cu disengages 2578 units; 1 equivalent Zn, 5857 units (Andrews). The reduction of N_2O_5 to N_2O_3 causes an absorption of 36,400 units (Thomsen).

Heat Developed During the Combination of Acids and Gases.—The chief workers in this field have been Hess, Andrews, Graham, Favre, Silbermann, Berthelot, and Thomsen. The experiments of Hess illustrate the general principle that in the formation of a chemical compound the heat developed is a constant quantity, being the same in amount whether the combination takes place directly at one time, or indirectly at repeated times. He concluded, however, that the same acid in combining with equivalents of different bases produced the same quantity of heat; a conclusion at direct variance to that arrived at by Andrews, and now generally accepted, that the heat developed during the union of acids and bases is determined by the base and not by the acid.

The following is an outline of the method pursued by Andrews in some of his latest experiments. The solutions were taken in so dilute a state that the heat disengaged never exceeded 3°·5 C. A standard solution of sulphuric acid was most carefully prepared, and the strength of the alkaline solutions adjusted by its means. The same solution of each alkali was employed in all the experiments, and the quantity used in each experiment determined by weighing. "The acid solution was of such a strength that after being mixed with the alkali an excess of 2 or 3 per cent. of acid was present. The alkaline solution was contained in a light glass vessel, in which a large platinum crucible holding the acid was carefully floated. By giving a rapid rotation by means of a light stirrer to the acid solution in the platinum crucible a perfect equilibrium of temperature was soon established between the two liquids. The initial temperature of the solutions was usually about 1°·5 below that of the air, and the final temperature of the mixture about 1°·5 above it. As the heat disengaged in the combination raised the liquid almost instantly to the maximum temperature, the whole correction required was for cooling. The first temperature was read one minute after the addition of the acid to the alkaline solution, the mixture being stirred during the whole of that time."

To measure the heat given off in chemical reactions Favre and Silbermann employ a kind of monster thermometer, the reservoir of which is made of iron, and contains a number of cylindrical openings, fitted with tubes of glass or platinum, in which the chemical reaction takes place. First the one substance is introduced and then the other. The heat developed in the combination expands the mercury filling the reservoir, and the mercurial column moves along the graduated tube constitu-

ting the stem of the instrument. By means of a screw the volume of mercury in the reservoir can be altered. By adjusting this screw the mercury is made to stand at the zero point of the instrument before an experiment is to be made. The instrument is graduated by experimenting with known weights of hot water. Although this apparatus is very convenient, yet, on account of the many errors to which it is liable, for accurate experimentation it is comparatively worthless.

The method of operating pursued by Andrews is far more accurate, and as a consequence his results have met with universal acceptation.

Andrews deduces the following conclusions from his experiments:—

1. The heat developed in the union of acids and bases is determined by the base and not by the acid, an equivalent of the same base, combined with different acids, producing nearly the same quantity of heat.

2. An equivalent of the same acid, combined with different bases, produces different quantities of heat.

3. When a neutral salt is converted into an acid salt by combining with one or more equivalents of acid, no disengagement of heat occurs.

4. When a double salt is formed by the union of two neutral salts, no disengagement of heat occurs.

5. When a neutral salt is converted into a basic salt, the combination is accompanied by the disengagement of heat.

6. When one and the same base displaces another from any of its neutral combinations, the heat evolved or absorbed is always the same, whatever the acid element may be.

7. As some of the bases (potash, soda, baryta, and strontia) form an isothermal group, such bases will develop the same, or nearly the same, heat in combining with an acid, and no heat will be developed during their mutual displacements.

For the first law to hold good the acid must have the power of neutralizing the alkaline reaction of the base, so that the acid and base when brought into contact may form a neutral solution. Hydrocyanic, carbonic, and arsenious acids which fail to fulfil these conditions, do not disengage the normal amount of heat when mixed.

These laws are not intended to embrace the thermal changes which occur during the conversion of an anhydrous acid and base into a crystalline compound. The steps by which such a conversion is effected are generally very complicated, and involve successive combinations and decompositions. Andrews found that sulphuric acid developed about one-eighth more heat, and a group of acids, comprising the tartaric, citric, and succinic acids, about one-thirtieth less heat, than the most of the other acids. All the other acids develop nearly the same amount of heat in combining with the same base, the greatest divergences from the mean being very slight, and within the limits of the errors of experiment. Favre and Silbermann have inferred from their experiments that the following organic acids—the oxalic, formic, valeric, and citric—disengage sensibly the same quantity of heat, but less in amount than that given by such mineral acids as nitric and hydrochloric. Andrews admits no such distinction between mineral and organic acids, inasmuch as he finds that oxalic acid disengages at least as much heat in combining with bases as the strong mineral acids, nitric and hydrochloric, &c. It actually disengages a little more heat than either of these acids when it combines with potash, soda, or ammonia. As to its thermal action oxalic acid stands in the same rank as the phosphoric, nitric, arsenic, hydrochloric, hydriodic, boracic acids, &c. The bases, on the contrary, differ altogether in thermal power. Thus, equivalents of the oxides of magnesium and of silver give out 4°·1 and 1°·8 of heat respectively in combining with nitric acid, the former oxide having therefore 2·3 times the thermal power of the latter. Neutralizing power has no apparent influence on the result, as oxide of silver, which forms salts neutral to test paper with the strongest acids, is one of the feeblest bases if measured by its thermal power.

When solutions of two neutral salts are mixed, and a precipitate formed by the double decomposition, there is always a slight disengagement of heat, perfectly definite in amount, which appears to be chiefly connected with the latent heat of the precipitate, and not to the change of state of its components; and the heat disengaged is greater when the precipitate contains water of crystallization. But notwithstanding the heat due to the formation of the precipitates, a diminution of temperature occurs when potash is substituted for lime or magnesia. In the conversion of the neutral sulphate of potash into the acid salt there is exceptionally a slight fall of temperature; and in the change of the ordinary phosphates and arseniates into super-salts, as might have been expected from their alkaline reaction, there is a disengagement of heat, about one-seventh of that liberated in the formation of the salts themselves. If tribasic phosphoric acid or arsenic acid is added in fractional portions to a solution of potash till the subsalts are formed, the heat given out on each addition of acid corresponds to the amount of acid added; but after this point has been reached, the disengagement of heat follows a different law. The pyrophosphoric acid, however, behaves as an ordinary acid, equal increments of heat being evolved for equal increments of acid till the pyrophosphate is formed.

In his seventh conclusion Andrews anticipates Thomsen of Copenhagen.

The following table gives Andrews' results reduced to the same units as those employed by Favre, Silbermann, and Thomsen. The absolute amount of heat obtained by Thomsen is much less than that obtained by Andrews; for example, in the combination of soda with nitric acid the number given by Thomsen is as much below Andrews' number as Favre and Silbermann's is above it. A. is for Andrews, F. & S. for Favre and Silbermann, and T. for Thomsen.

	Potash.		Soda.			Ammonia.	
	A.	F. & S.	A.	F. & S.	T.	A.	F. & S.
Sulphuric,	16,701	16,083	16,580	15,810	15,689	14,710	14,690
Nitric,	14,800	15,510	14,480	15,283	13,617	12,683	13,676
Hydrochloric,	14,940	15,656	14,744	15,128	13,740	12,964	13,536
Oxalic,	15,124	14,156	15,032	13,752		13,088	—
Acetic,	13,805	13,973	14,000	13,600		12,316	12,649
Tartaric,	13,508	13,425	13,400	13,651		11,744	—

Some of Thomsen's results are contained in the following tables, where is given the quantity of heat in hundreds of gram. degrees, produced by 1 molecule of each of the acids or alkalies upon *a* molecules of the alkali or acid respectively:—

	1 Molecule of Acid with *a* Molecules of Sodium Hydrate.			1 Molecule of Sodium Hydrate with *a* Molecules of Acid.			
	½ *a*	1 *a*	2 *a*	½ *a*	⅓ *a*	1 *a*	2 *a*
1. *Monobasic acids*—							
Hydrochloric,	68·5	137	137	—	68·5	137	137
Hydrobromic,	68·5	137	137	—	68·5	137	137
Hydriodic,	68	137	137	—	68·5	137	136
Hydrocyanic,	14	28	27	—	14	28	28
Nitric,	68	137	137	—	68	137	136
Metaphosphoric,	71	144	—	—	—	144	142
Acetic,	66	132	132	—	66	132	132
2. *Dibasic acids*—							
Sulphuric,	71	146	310	78	155	146	142
Sulphurous,	—	159	290	73	145	159	—
Carbonic,	—	110	202	51	101	110	—
Chromic,	—	131	247	63	124	131	—
Silicic,	32	43	52	13·5	26	43	65
Oxalic,	69	138	283	71	141	138	138
Tartaric,	—	124	253	—	127	124	—
3. *Tribasic acids*—							
Citric,	—	124	250	—	125	124	—
Orthophosphoric,	73	148	271	—	135	148	147
Arsenic,	74	150	276	—	138	150	147
4. *Tetrabasic acid*—							
Pyrophosphoric,	—	144	286	132	143	144	—

Thomsen draws these conclusions:—1. When 1 molecule of an acid acts upon a solution of sodium hydrate, the heat evolved is nearly proportional to the quantity of soda until this amounts to 1, 2, or more molecules, according to the basicity of the acid.

2. When 1 molecule of sodium hydrate acts upon an acid, the heat evolved is nearly proportional to the quantity of acid until this amounts to ¼, ⅓, ½, or 1 molecule, according to the basicity of the acid.

3. With well-marked acids an excess of the acid or alkali produces very slight thermal effects.

Boric, orthophosphoric, and arsenic acids are exceptions to the above conclusions.

Berthelot regards *weak* acids as being characterized by imperfect combination, and by the division of the base of a salt between the acid and the water. *Strong* acids and bases, on the other hand, form neutral stable salts, such as the sulphate or chloride of sodium, which are not modified by excess of base or decomposed by water. When a weak acid combines with a strong base, such as ammonia, neutral salts are formed, which are partially decomposed by water. According to Berthelot, the mixing of two neutral stable salts is always accompanied with a slight evolution or absorption of heat, in which Marignac agrees with him. Such salts as the sulphides of the alkalies are completely decomposed by water into sulphydrates and free alkali. In these double decompositions the most stable compound is always formed in largest quantity. Berthelot has also examined the thermal effects produced in double decompositions without secondary products, as in the decomposition of the chlorides of acid radicles by water and alkalies. The decomposition of 1 equivalent (78·5 grams.) acetyl chloride by water gave 23,300 heat units. Deducting from this the heat of solution of 1 equivalent each of hydrochloric acid gas and glacial acetic acid, we obtain 5500 units as the heat due to the reaction. The decomposition of acetyl bromide was equal to 18,000, and of acetyl iodide, to 1800 units.

Thermal Effects of the Combination of Alcohols with Bases.—The reaction of glycerin upon the alkalies produces about the one-fortieth part of the heat evolved by the combination of an acid with a base. The heat increases with the number of equivalents of glycerin added, but not proportionally; and it diminishes as the dilution becomes greater. When alcohols combine with acids or bases the amount of combination appears to depend upon the quantity of water present. The alcoholic acids in combining with bases show their acid character by the evolution of a quantity of heat proportional to the quantity of base added, and independent of the amount of water present, and their alcoholic character by the rapid diminution of the thermal effects on dilution with water (Berthelot).

Heat Disengaged During Metallic Substitutions.—When a neutral solution of any salt, say of the black oxide of copper, as the sulphate, chloride, or acetate, is precipitated by metallic zinc, the final result is the substitution of an atom of zinc for an atom of copper in the solution, and the precipitation of an atom of copper. Andrews establishes as the result of his investigations the general principle that when an equivalent of a metal A displaces an equivalent of another metal B from a solution of any of its salts, the heat developed is with the same metals constantly the same whatever be the nature of the salt, provided that in all the salts B is in the same state of oxidation. Andrews' general method was to mix a known weight of the finely-divided metal with the salt to be decomposed, having the metal in excess, and to note carefully the increase of temperature.

TABLE OF HEAT EVOLVED IN METALLIC SUBSTITUTIONS (ANDREWS).

	One Equivalent Precipitated Metal.
Salts of copper and zinc,	3435°
" " and iron,	2342°
" " and lead,	1061°
" silver and zinc,	5747°
" " and copper,	2176°
" lead and zinc,	2357°
" platinum and zinc,	11085°
" mercury and zinc,	4166°

We have thus a means of arranging these metals, beginning with the one that evolves most heat when used to displace the metal at the other extremity of the series.

1. Zinc.	5. Mercury.
2. Iron.	6. Silver.
3. Lead.	7. Platinum.
4. Copper.	

This is exactly the electro-chemical order of the metals.

Andrews also deduces the following conclusion:—"If three metals, A, B, C, be so related that A is capable of displacing B and C from their combinations, and also B capable of displacing C; then the heat developed in the substitution of A for C will be equal to that developed in the substitution of A for B, added to that developed in the substitution of B for C; and a similar rule may be applied to any number of metals similarly related." Thus—

1 equivalent lead displaced by zinc,.....	2357°
1 equivalent copper, by lead,.....	1061°
	3418°

Experiment gives instead 3435°, which corresponds closely with the theoretical number. So also an equivalent of mercury displaced by zinc should give 731 units of heat; of platinum displaced by copper, 7650 units; by mercury, 6919 units, &c. "Compare this with the fact that the electro-motive force between A and C is equal to that between A and B, *plus* that between B and C; and we are led to imagine that the electro-motive forces which are really due to contact of dissimilar bodies are also the very forces which cause heat when chemical combination ensues, potential energy being then converted into kinetic energy by the rushing together of the particles under the attracting forces" (Stewart).

Specific Heat.—The temperature of a body affords no indication of the actual quantity of heat it contains, as equal bulks of different kinds of matter contain different amounts of heat. Bodies require various quantities of heat to raise their temperatures equally, and disengage unequal quantities in cooling through the same number of degrees. This different *capacity* for heat is called *specific heat.*

If a litre of water at 100° C. is mixed with a litre at 40° C., the resulting temperature will be the mean of the two, 70° C.; but if a litre of mercury at 100° C. be added to the litre of water at 40° C., the temperature of the mixture will be 60° C. The mercury therefore gives up less heat than a corresponding volume of water, and accordingly is said to have a less capacity for heat. If equal weights instead of equal volumes be mixed, the difference in capacity will be made more evident. Mix a kilo. of mercury at 20° C., with an equal weight of water at 54° C., and the resulting temperature will be 53° C.; the 1° of temperature that the water has lost has been sufficient to raise the kilo. of mercury through 33°.

The quantity of heat which it is necessary to supply to a unit weight of substance to raise its temperature from t° to t + 1°, is called its specific heat at t°; and water being taken as the standard of comparison, the specific heat of a body is said to be the quantity of heat required to raise it 1° C. (from 0° to 1° C.), as compared with the amount required to raise an equal weight of water 1° C. Maxwell defines it to be the ratio of the quantity of heat required to raise the body 1° to the quantity required to raise an equal weight of water 1°.

The numbers obtained by experiment as the specific heats of bodies must be corrected for all the heat not employed in raising the temperature of the body, but used up in internal and external work during the process. Every change of constitution, chemical, physical, or mechanical, causes an absorption or evolution of heat, as the case may be. The true specific heats are only approached in the determination of the specific capacity of the perfect gases at constant volume, as there is then no external work done, and the internal work is very slight.

Methods for Determining Specific Heat.—There are three general methods employed for determining the specific heat of a body—1st., the method by mixture; 2nd., the method by cooling; and 3rd., the method by fusion of ice.

I. *The Method by Mixture.*—This name is given to all the processes where the heat that escapes from one body is measured by the rise in temperature it occasions in the body into which it passes.

A body of known weight, w, is raised to T°, and then immersed in a quantity of water, W, at t° contained in a calorimeter. In the water is fixed a very sensitive thermometer. The body parts with its heat to the water, which is warmed from t° to its maximum temperature, θ, the body cooling at the same time from T to θ. The body loses $w\,x\,(T-\theta)$, and the water gains $W\,(\theta - t)$. Therefore

$$W\,(\theta - t) = w\,x\,(T-\theta)$$
$$\therefore\ x = \frac{W\,(\theta - t)}{w\,(T-\theta)}$$

But heat is also gained by the calorimeter, by the glass and mercury of the thermometer, and by the agitator; and if the body is provided with an envelope it also will furnish part of the heat given out. The equation would therefore have to be written so as to express that the quantity of heat given up by the body and its envelope, if it have one, is equal to that gained by the water, the calorimeter, the thermometer, and the rod. To find x we must know the specific heats of all these.

Let W = weight of body, T = its initial temperature, x = its specific heat; m = weight of envelope, a = its specific heat; W′ = weight of water in calorimeter, w = weight of calorimeter, c = its specific heat; w′, w″, w‴ = weights respectively of glass of thermometer, mercury, and rod, and c′, c″, c‴ = their specific heats. Then—

$$W\,x\,(T-\theta) + m\,a\,(T-\theta) =$$
$$(W' + w\,c + w'c' + w''c'' + w'''c''')\,(\theta - t)$$

whence—

$$x = \frac{(W' + w\,c + w'c' + w''c'' + w'''c''')\,(\theta - t) - m\,a\,(T-\theta)}{W\,(T-\theta)}$$

In addition to these corrections the loss of heat by radiation during the experiment must be taken into account. Rumford introduced a method of compensation which consisted in lowering the initial temperature of the calorimeter as many degrees below that of the surrounding air as the final temperature is above it.

Kopp makes use of a thin glass tube, into which he introduces the body whose specific heat is required. The tube and its contents are heated in a mercurial bath at or about 50° C.; they are then transferred at once to a small calorimeter containing a known weight of cold water, and the rise of temperature determined. The calorific effect of the tube itself is ascertained by a separate experiment. Deducting this from the preceding result the data are obtained for calculating the specific heat of the body.

If the body is solid it is reduced to fragments, and placed in the tube with naphtha, or some liquid that will not dissolve it. As before, the correction for the tube and naphtha must be determined by a separate experiment.

The method by mixture is due to Black; it was practised by Dulong and Petit, and perfected by Pouillet, Neumann, Regnault, and Kopp.

II. *Method by Cooling.*—This method was employed by Mayer, Böekmann, Dulong and Petit, Hermann, De la Rive and Marcet, &c. Those bodies that possess the greatest capacity for heat are the slowest in cooling, and it is upon this principle that the method depends. Equal weights of the different bodies, whose specific heats are required, are allowed to cool down through a definite number of degrees (as from 100° C. to 15° C.) under the same conditions as an equal weight of water. The heated substance is placed in a thin copper vessel whose outer surface is blackened. A larger copper vessel surrounds this, and is itself fixed in a bath of water kept at a constant temperature. Taking the time required by the water in cooling as the unit of comparison, a series of numbers will be obtained, representing approximately the specific heats of the bodies, by comparing the time occupied by each in cooling with the time occupied by the water.

The thermal value of radiation at any temperature is expressed by Dulong and Petit in this form—

$$R = m a^{\theta},$$

R = total loss of heat in unit of time by radiation from unit of area at temperature θ in centigrade degrees; m = a constant depending on the substance and the nature of its surface; a is a numerical quantity = 1·0077.

If the body is placed in a perfectly exhausted vessel of a temperature t, the heat radiated and absorbed (r) will be $= m a^{t}$; making the actual loss of heat $R - r = m a^{\theta} - m a^{t}$.

The method by cooling offers the advantage of being simple in practice; but it has the inconvenience of being very indirect. It is more accurate for liquids than solids, as with solids there are the disturbing influences of radiation, unequal conducting power, &c.

III. *Method by Fusion of Ice.*—Wilcke was the first to employ the melting of snow in the determination of the heat given out by bodies in cooling. Black used a calorimeter made of a block of ice. In this he cut a cavity, and fitted it with an ice cover. When the cavity was carefully dried and covered, it remained dry, as the external heat was arrested by its walls. The substance whose specific heat was required was then heated to T degrees, and projected into the cavity. At the end of some time the body was cooled to zero. The ice melted was carefully wiped up with a weighed piece of linen, and its increase in weight gave the weight of the ice melted. Let W be the weight of the body; x, its specific heat; w, the weight of ice melted. In cooling the body has lost W x T heat, and the ice melted has gained w 79·25; therefore W x T = w 79·25 (79·25 = the latent heat of water).

Laplace and Lavoisier adopted the same method, but they replaced the block of ice by an apparatus consisting of three vessels, one within another. The innermost vessel, made of thin sheet copper, held the heated body. The second vessel surrounded this, and the space between was filled by broken ice. The melted ice was allowed to trickle through a drainer into a receiver placed beneath. The third vessel entirely surrounded the last, all the intervening space being filled with ice, so that it acted as an ice jacket, and prevented any external heat from entering the ice contained in the second vessel, which was the calorimeter proper. The heated body was placed in the innermost vessel, and parted with its heat to the ice in the middle vessel; and by measuring the water produced by the melting of the ice, the heat that escaped was estimated. It is impossible, however, with this apparatus to determine accurately the amount of ice melted, on account of the water adhering to the fragments of ice, &c.

In Bunsen's calorimeter the quantity of ice melted is estimated by the contraction which the volume of the whole undergoes, as a given weight of ice at 0° occupies a larger volume than the same weight of water at 0° C. Sir J. Herschel had previously suggested the same method.

IV. *Additional Methods.*—Gases inclosed in a manometer and exposed to the same source of heat require different times to expand to the same volume. De la Rive and Marcet made use of this as a method for determining the specific heat of gases.

Another method consists in causing the gases to blow into an organ pipe, and determining the pitch of the note thus produced. But this method is not practicable at high temperatures.

Specific Heats of Solids, Liquids, and Gases.—In his determinations of the specific heat of solids, Regnault used the method by cooling, and reduced the substance to a fine powder. He found that the specific heat of the same substance in the solid state depends to some degree on the mechanical treatment it has received.

The specific heats of solid organic bodies are very

difficult to measure. Those of organic liquids can be determined much more easily by the method of cooling. As they vary so much with the temperature, it is impossible to formulate any law of general application.

Pictet deduces a relation between the latent and specific heats of a liquid, the latent heat always being a multiple of the specific heat. Reference may here be made to the relationship he has shown to exist between the latent heats of liquids at the same pressure, and referred to a uniform temperature, and their molecular weights; the product of the latent heat and the molecular weight being constant, as is also the product of the molecular weight and the difference between the latent heats at any two temperatures.

The determination of the specific heat of a gas involves great difficulty. The gas must be inclosed in a vessel, and as the density of the gas is so slight, its specific heat forms but a small part of the total heat capacity of the apparatus. Till Regnault's time the numbers obtained were very inaccurate. His great experimental skill alone enabled him to obtain trustworthy results. The plan adopted by him was a modification of that already used by Delaroche and Bérard. The gas was first condensed in a strong receiver, and a known weight allowed to escape in a continuous stream, with a constant velocity and at a constant pressure, through a spiral tube fixed in a vessel of hot oil, maintained at a regular temperature. The heated gas was next passed through a calorimeter containing a certain weight of water at a known temperature. In this way large quantities of gas were experimented on. From the rise in temperature of the water the specific heats for *equal weights* of the different gases can be calculated; and by multiplying the numbers for equal weights by the specific gravities of the respective gases, the specific heats are obtained for *equal volumes*. For air Regnault obtained a specific heat = 0·2379; but Rankine, by applying thermodynamic principles to facts previously known, had already estimated it as = 0·2378, showing a very close agreement with Regnault's result obtained by direct experiment.

The specific heat of a gas is the same at all pressures and temperatures, and all simple gases have nearly the same thermal capacity for unit volume. The volume of a gas will increase in arithmetical progression if equal quantities of heat be successively added to it. The specific heats of the simple incondensible gases for equal volumes are nearly the same, but for equal weights there is considerable difference. Hydrogen has the highest specific heat of all known substances, its co-efficient being 3·4·09 if the comparison be for equal weights.

On page 882, vol. I., will be found a short table giving the specific and atomic heats of the more important elementary bodies.

The comparison of these specific heats shows that there is not the same regularity among the metalloids as among the metals; antimony, selenium, solid bromine, solid iodine, sulphur, and phosphorus giving products nearest approaching the mean of the metals, 6·4, while silicon, boron, and carbon exhibit the widest divergence.

SPECIFIC HEATS OF GASES AND VAPOURS (AFTER REGNAULT).

	For Equal Volumes.	For Equal Weights.
Air,	0·2374 0·2389 (Wiedemann)	0·2374
Oxygen,	0·2405	0·2175
Nitrogen,	0·2368	0·2438
Hydrogen,	0·2359	3·4090
Chlorine,	0·2964	0·1210
Bromine,	0·3040	0·0555
Nitrous oxide,	0·3447 0·3014 (Wiedemann)	0·2262
Nitric oxide,	0·2406	0·2317
Carbonic oxide,	0·2370 0·2346 (Wiedemann)	0·2450
Carbonic anhydride,	0·3307 0·2985 (Wiedemann)	0·20246
Carbonic disulphide,	0·4122	0·1569
Ammonia,	0·2996 0·2952 (Wiedemann)	0·5083
Marsh gas,	0·3277	0·5929
Ethylene,	0·4160	0·4040
Sulphurous anhydride,	0·3414	0·1553
Hydrochloric acid,	0·2333	0·1852
Sulphuretted hydrogen	0·2857	0·2432
Water,	0·2989	0·4805
Alcohol,	0·7171	0·4534
Ether,	1·2266	0·4796
Chloroform,	0·6461	0·1567
Benzol,	1·0114	0·3754
Acetone,	0·8244	0·4125
Spirits of turpentine,	2·3776	0·5061

SPECIFIC HEATS OF LIQUIDS AND VAPOURS COMPARED (AFTER REGNAULT).

	Liquid.		Gaseous.	
	Specific Heat.	Temperature C.	Specific Heat.	Temperature C.
Water, H_2O,	1·0000	Between 11° and 100°	0·4805	Between 128° and 220°
Bromine, Br_2,	0·1060 0·1129	— 29° " 11° 13° " 58°	0·0555	83° " 228°
Alcohol, C_2H_6O,	0·505 0·7694	— 20° " 80°	0·4534	105° " 220°
Ether, $C_4H_{10}O$,	0·5113 0·5467	— 30° " 30°	0·4797	70° " 228°
Chloroform, $CHCl_3$,	0·2293 0·2354	— 30° " 30°	0·2293	111° " 221°
Benzol, C_6H_6,	0 4360	— 20° " 71°	0·3754	116° " 218°

Causes of Alteration of Specific Heat.—I. *Influence of Changes of Density.*—The specific heat of a body is not an unchangeable constant, but varies according to the special conditions in which it

is found. Anything that alters the relative distances of its molecules alters its specific heat. In general whatever augments the density diminishes the specific heat, and *vice versa*. Thus mechanical compression, by increasing the density, produces a corresponding decrease in the specific heat.

Solids.—Soft well annealed copper has a specific heat of ·09501; after being well hammered, a specific heat of ·0936; and on being reannealed a specific heat of ·09493, almost what it was at first. But soft steel, the density of which at 14° C. is 7·8609, has a specific heat of ·1175; hard steel, having a density of 7·7982, has also a specific heat of ·1175. In dimorphous bodies the densest has usually the lowest specific heat. The more carbon is divided, for example, the greater is its specific heat.

Animal charcoal,	0·2608
Wood,	0·2415
Coke,	0·2008
Graphite,	0·2018
Diamond,	0·1468

(Regnault).

The specific heat of a compound is diminished by increasing its density; thus, peroxide of iron and protoxide of nickel have their specific heats diminished by strong ignition.

Gases and Vapour.—Sudden compression of aeriform bodies is attended with the evolution of a very large amount of heat, and their rarefaction is attended with the opposite result. Delaroche and Bérard believed that the specific heat of gases varied with the pressure, but Regnault has shown that it is independent of it. The absorption of heat that attends expansion he has proved not to be due to an alteration of specific heat. The effect of pressure really is that the specific heat of a given *volume* of a perfect gas increases directly with its density; while for *equal weights* it varies neither with pressure nor density.

II. *Influence of Temperature.—Solids.*—The capacity for heat of any given body increases with its temperature. Those metals whose rate of expansion increases most rapidly when heated likewise increase most in specific heat (Dulong).

	Between 0° and 100° C.	Between 0° and 300° C.
Iron,	0·1098	0·1218
Mercury,	0·0330	0·0350
Zinc,	0·0927	0·1015
Silver,	0·0557	0·0611
Copper,	0·0949	0·1013
Platinum,	0·0355	0·0355
Glass,	0·1770	0·1900

The variation of the specific heat with the temperature is much more rapid the nearer the body is to its melting point. Spring finds that the variations in the specific heat of alloys are independent of the temperature, but follow those of volume. When bodies are heated they usually expand and their specific heat increases; but when instead of expansion there is contraction, the specific heat diminishes. The specific heat is probably therefore a function of the volume rather than of the temperature (Spring).

Liquids.—The general rule is that the specific heat increases with the temperature, and at a more rapid rate than in the case of solids. It was formerly thought that water had the greatest capacity for heat of any liquid, but Dupré states that the specific heat of a mixture of alcohol 20 per cent. and water is 1·05 (water = 1·00).

The specific heat of water has an important scientific value, as it is taken as the unit of comparison. But, as is seen in the following table, water like other liquids increases in specific heat with rise of temperature; accordingly the unit is taken to be the quantity of heat required to raise 1 kilo. of water from 0° to 1° C.

Specific heat of water (Regnault).

$C = 1 + 0{\cdot}00004\,t + 0{\cdot}0000009\,t^2$

t = 0	C = 1
50	1·0042
100	1·0132
150	1·0262
200	1·0444
230	1·0568

Organic Liquids.—Their specific heat rises rapidly with rise of temperature. For equal weights it decreases as the molecular weight of the substance increases. When the products obtained by multiplying the specific heat into the molecular numbers are compared, they are found generally to increase with the molecular weight. In the homologous series of the alcohols, fatty acids, and ethers, this increase is about 7 for each addition of CH_2 in the molecule of the compound.

Gases and Vapours.—Contrary to the opinion held by Delaroche and Bérard, Regnault concludes that the specific heat of air does not increase with rise of temperature, at least between —30° and 200° C.; and the same holds good for gases that are not readily liquefied. The specific heat of carbonic anhydride, ammonia, and nitrous oxide—condensible gases—on the contrary, increases with the temperature—

			Regnault.		Wiedemann.
Carbonic anhydride,	0°C	specific heat	= ·1870	....	·1952
	100°C	"	= ·2145	....	·2169
	200°C	"	= ·2396	....	·2387
			Wiedemann.		
Ammonia,	0°	"	= ·5009	....	—
	100°	"	= ·5317	....	—
	200°	"	= ·5629	....	—
Nitrous oxide,	0°	"	= ·1983	....	—
	100°	"	= ·2212	....	—
	200°	"	= ·2442	....	—

With vapours the increase in the specific heat is still greater. But this increase in specific heat cannot be explained in the case of these gases by their deviation from perfect gaseity. Ammonia is not so perfect a gas as carbonic anhydride or nitrous oxide, yet its specific heat varies less with temperature than either of these two gases. Probably a gradual dissociation of molecules occurs with increased temperature, and thus causes an absorption of heat.

III. *Influence of Physical State.*—The specific heat of a body is lowest in its gaseous form, approaching sensibly the capacity it possessed as a solid, and is greatest when in the liquid form. The

difference is well seen in the case of water—water, specific heat = 1; ice, ·5050; steam, ·4805.

SPECIFIC HEATS OF THE SAME BODY IN THE SOLID AND LIQUID FORMS.

	Solid (Regnault).		Liquid (Person).	
	Sp. heat.	T° C.	Sp. heat.	T° C.
		Between.		Between.
Ice,	0·5050	—30° and 0°	1·0000	0° and 20°
Sulphur,	0·2026	0° " 100°	0·2340	120° " 150°
Phosphorus,	0·1788	—14° " 7°	0·2045	50° " 100°
Bromine,	0·0483	—78° " 20°	0·1060	—12° " 48°
Tin,	0·0562	0° " 100°	0·0637	250° " 350°
Iodine,	0·0541	"	0·1082	—
Lead,	0·0314	"	0·0402	350° " 450°
Bismuth,	0·0308	"	0·0363	280° " 380°
Mercury,	0·0309	"	0·0333	0° " 100°

Specific Heat at Constant Pressure and at Constant Volume.—In the case of gases we distinguish two kinds of specific heat—specific heat at constant pressure and specific heat at constant volume. The first is the quantity of heat required to raise the temperature of a unit weight of the gas by one degree, when the gas is allowed to expand without any change of pressure; the second is the amount of heat required to raise the temperature of the unit weight of a gas one degree, when the gas is prevented from expanding, and its volume remains the same. In the latter case the specific heat is less. Oxygen, for example, has a specific heat of ·2175; but if prevented from expanding, that is, kept at a *constant volume*, it will only be five-sevenths of this, or ·15; of hydrogen, the specific heat is 3·409, but at constant volume five-sevenths of this, or 2·435. So that, when allowed to expand, these gases require two-sevenths more heat in being raised 1° C. than if heated without being allowed to expand.

The ratio of the specific heat at constant pressure to that at constant volume is equal to the ratio of the elasticity when no heat escapes, to the elasticity at constant temperature. For all simple gases the ratio of the two specific heats is constant, having a value equal to 1·41. The ratio, however, would be 1·66 on the thermodynamic theory of gases if the molecules of the gas were only affected by movements of translation. Kundt and Harburg deduced the ratio of the two specific heats for the vapour of mercury by measuring the distance of the nodes in pipes made to sound with air and the vapour of mercury respectively. The number they obtained was 1·67.

The ratio is not constant with liquefiable gases and vapours: ammonia, ratio = 1·328; carbonic anhydride, 1·29; ether vapour, 1·079.

The following example will illustrate the difference between the two specific heats. A cubic foot of air, which weighs at 0° C. 1·29 oz., supports a pressure of 15 lbs. to the square inch, that is, $144 \times 15 = 2160$ lbs. If heated through 272° C. its volume will be doubled; and it will have raised the superincumbent weight of 2160 lbs. through one foot, and thus done 2160 foot-pounds of work. The specific heat of air is 0·237, and accordingly the heat required by the air in passing from 0° to 272° will be: $\frac{1·29}{16} \times 0·237 \times 272 = 5·19$ heat units. In this increase of temperature, work equal to 2160 mechanical units has been done; and adopting Joule's unit of 1390 foot-pounds as the mechanical equivalent of heat, this work is equal to $\frac{2160}{1390} = 1·554$ heat units: 1·554 of the 5·19 heat units have therefore been spent in work, and only 3·636 units in the elevation of temperature. Now, if the gas had been prevented from expanding and thus doing work, only 3·636 units would have been needed. Hence the specific heat of air at *constant volume* is $= 0·237 \times \frac{3·636}{5·19} = ·166$.—(Stewart.)

Relation of Specific Heat to Atomic Weight.—I. *Elementary Bodies.*—Dulong and Petit were the first to establish a relationship between the atomic weights and specific heats of the elementary bodies. They deduced the law that the specific heats vary inversely as the atomic weights. An atom of one element then requires the same amount of heat as the atom of any other element to raise its temperature through a given number of degrees. Of course, the greater the atomic weight of any substance the smaller will be the number of atoms of it required to make up a given absolute weight. It follows, therefore, that the product of the atomic weight and specific heat will give the capacity for heat referred to a given number of atoms. This product is termed by Regnault the element's *atomic heat.* The mean atomic weight found by him for such bodies as aluminium, cadmium, iron, mercury, lead, zinc, tin, &c., was 3·13; and for such as gold, silver, thallium, lithium, potassium, antimony, bismuth, phosphorus, &c., 6·24. He proposed to halve the old atomic weights of the latter class, but it has been found more convenient to double those of the first class.

a. Solids and Liquids.—By the table on page 882, vol. i., it will be seen that the atomic heats are practically equal, on condition, of course, that the atomic weights formerly assigned to certain of the elements are doubled. With the metals the relation is a simple one, because here the comparison is made among bodies in analogous conditions. But with the metalloids we do not notice the same regularity, as they cannot well be compared under similar conditions. Antimony, tellurium, and selenium resemble the metals very closely, and accordingly their atomic heats are close upon 6·4. Solid bromine, iodine, sulphur, and phosphorus also do not differ widely. But bromine possesses a heat too high in the liquid, and too low in the gaseous form; sulphur at ordinary temperatures is less than 6·4; and boron, silicon, and carbon, much less.

Exceptions to the Law.—Most of the differences in the atomic heats may be due to certain disturbing causes. Some bodies, it may be noticed, are difficult to obtain pure; and as Regnault has observed, the determination of the specific heat of solid bodies involves some uncertainty, as it includes the latent

heat of dilatation—a portion of the latent heat of fusion, which bodies successively absorb as they soften, frequently long before their fusing points. Although the law does not yield the rigidly accurate results stated by Dulong and Petit, yet the only real exceptions appear to be carbon, silicon, and boron, bodies which exhibit peculiar phenomena of allotropy, their particles being capable of grouping themselves in different ways. When such a body is subjected to the action of heat a movement of its particles may take place, and in the internal work thus done a certain quantity of heat may be evolved or absorbed. It is just this quantity of heat that may account for the exceptions to Dulong and Petit's law; and there is every reason for believing that the differences are due to some peculiarity in the molecular constitution of the bodies in the free state. The different forms of carbon possess different thermal equivalents; and between them and the atomic weight of carbon (12) there exists no apparent simple relation. The mean atomic heat we may take as 6·4. Dividing this constant by the specific heats of carbon, we obtain—

	Spec. Heats.	Thermal Equiv.	Atomic Weight.
Animal charcoal,	0·26086	24·5	12
Graphite,	0·200	32·0	
Diamond,	0·147	43·5	

Carbon in combination would therefore appear to possess a different specific heat from what it has in its modifications. Schröder supposes that certain substances may have different atomic heat capacities according to the compounds in which they exist. He connects this alteration of heat capacity with the change in the body's equivalent volume, the specific heat being smallest in that compound into which it enters with the smallest equivalent volume. Kopp suggests that the metals and all the so-called elements which have the atomic heat of 6·4 may possibly be compounds; whilst the diamond, whose atomic heat is only 1·8, may be really the only elementary substance known to us.

Weber, however, maintains that carbon, boron, and silicon form no real exceptions to the law, as their specific heats increase rapidly with the temperature, until a point is reached when no further augmentation occurs. The specific heat at this limit he regards as the true specific heat.

	Specific Heat.	Atomic Weight.	Atomic Heat.
Silicon,	0·203	28	5·7
Carbon,	0·467	12	5·6
Boron,	0·5 (?)	11	5·5 (?)

(Weber).

b. Gases.—The capacities for heat of simple gases are identical for equal volumes (Delaroche and Bérard); but Regnault has shown that this law is only applicable to gases which obey Boyle and Mariotte's law.

The simple and incondensible gases appear to possess a mean atomic heat of 2·4; chlorine and bromine are not perfect gases, as they are easily condensed, and their atomic heat is higher.

	Atomic Weight.	Spec. Heats Constant Vol.	Product of Atomic Weights and Specific Heats.
Hydrogen	1	2·411	2·4
Nitrogen,	14	0·173	2·4
Oxygen,	16	0·155	2·48
Chlorine,	35·5	0·093	3·3

(Regnault).

There is also an equality in the atomic heats of compound gases that are formed without condensation, such as hydrochloric acid (Dulong).

If we compare the atomic heats of different gases we find they present anomalies almost inexplicable, unless we take into consideration the grouping of the atoms. Thus, hydrochloric acid gas, nitric oxide, and carbonic oxide, which have a similar molecular constitution, show an atomic heat nearly identical, and equal to twice that of the simple gases (about 4·8). Water, sulphuretted hydrogen (H_2S), nitrous oxide (N_2O), carbonic anhydride (CO_2), and sulphurous anhydride (SO_2) also are closely allied, and have an atomic heat about three times that of the simple gases. But then again in marsh gas and ammonia the atomic heat is only about two-thirds of what it should be by calculation. The quantity of heat absorbed by internal molecular work in gases, though much less than with solids and liquids, is therefore a disturbing cause, and until it is eliminated we cannot determine the true specific heats.

II. *Compound Bodies.*—Neumann showed that in the case of the sulphates and carbonates the products of the specific heats by the chemical equivalents remain constant when we replace one base by the other. By Hermann it was pointed out that the heat capacity of the compound atom in certain sulphides might be found by taking the sum of the capacities of the metal and of sulphur. Neumann's law was generalized by Regnault. As the general result of the latter's experiments, it may be stated that for compound bodies with the same formula and the same chemical constitution the product of the total equivalent by the specific heat is the same. Regnault gives the law thus—"The specific heats of compound bodies having the same chemical formulæ are to one another in the inverse ratio of their equivalents." The products of the specific heat of these bodies by their atomic weights—that is, their *atomic heat*—are sensibly equal, so that it may be said that they possess the same atomic heat (Kopp). Upon comparing the atomic heats of a large number of compound bodies, they are found to be formed by the sum of the atomic heats of their elements, being practically equal to $n \times 6{\cdot}4$, where n is the number of elementary atoms present.

The specific heat of an alloy is exactly equal to the mean of the specific heats of the metals of which it is composed (Regnault). Oxides and highly oxidated compounds, such as nitrates and chlorates, sulphides also, and sulphates, have always a molecular heat much less than 6·4, and the difference increases with the number of oxygen or sulphur atoms in the molecule. Wöstyn and Kopp consider that the simple bodies have the same capacity for heat whether they are combined or free, and that the atoms in

their solid combinations possess the specific heat of the solid form. Solid sulphur would then have a specific heat of 5·2; solid oxygen, 4·4; carbon, 1·8; hydrogen, 2·3; and silicon, 4.

SPECIFIC AND ATOMIC HEAT OF ORGANIC LIQUIDS (ANDREWS, FAVRE, SILBERMANN, KOPP, AND REGNAULT).

Compound.	Empirical Formula.	Molecular Weight.	Specific Heat of Equivalent Weights.	Atomic Heat.
Wood spirit,	CH_4O	32	·613	20·64
Formic acid,	CH_2O_2	46	·536	24·65
Sulphide of carbon	CS_2	76	·2206	16·77
Alcohol,	C_2H_6O	46	·615	28·29
Acetic acid,	$C_2H_4O_2$	60	·508	30·54
Acetone,	C_3H_6O	58	·530	30 74
Methyl acetate,	$C_3H_6O_2$	74	·513	37·96
Formic ether,	$C_3H_6O_2$	74	·485	35·89
Ether,	$C_4H_{10}O$	74	·517	37·22
Acetic ether,	$C_4H_8O_2$	88	·474	41·71
Butyric acid,	$C_4H_8O_2$	88	·503	45 30
Ethyl,	$C_4H_8O_2$	88	·496	43·65
Amylic alcohol,	$C_5H_{12}O$	88	·564	49·63
Benzol,	C_6H_6	78	·450	35·10
Nitro-benzol,	$C_6H_5NO_2$	123	·3499	43·04
Naphthaline,	$C_{10}H_8$	128	·4159	53·20
Oil of turpentine,	$C_{10}H_{16}$	136	·467	63·51
Terebenthine,	$C_{10}H_{16}$	136	·4267	57·93

Organic bodies of the formula C_nH_{2n}, with boiling points between 200° and 210°, have a specific heat = ·494 from 20° to 200° C.; while bodies of the same formula with boiling points from 240° to 260° have a specific heat = ·497 between 20° and 240° C. (Favre and Silbermann).

ATOMIC HEAT OF COMPOUNDS.

Class of Compounds.	General Formula.	Spec. Heat × Atom. Weight.	Atomic Heat.
Protoxides (as PbO),	$M^{ii}O$	11·30	5·65
Sesquioxides,	$M^{iii}{}_2O_3$	27·15	5·43
Dioxides,	$M^{iv}O_2$	13·84	4·61
Trioxides,	$M^{vi}O_3$	18·98	4·74
Sulphides,	M_2S	18·88	6·29
Sesquisulphides,	$M^{iii}{}_2S_3$	29 77	5·95
Disulphides,	$M^{iv}S_2$	20·8	6·93
Chlorides,	MCl	12·69	6·34
Dichlorides,	$M^{ii}Cl_2$	18·72	6·24
Trichlorides,	$M^{iii}Cl_3$	30·36	7·59
Bromides,	MBr	13·70	6·85
Dibromides,	$M^{ii}Br_2$	19·36	6·45
Iodides,	MI	13·46	6·73
Biniodides,	$M^{ii}I_2$	19·35	6·45
Nitrates,	MNO_3	24·137	4·82
Chlorates,	$MClO_3$	25·68	5·13
Sulphates,	M_2SO_4	33·04	4·72
Carbonates,	M_2CO_3	29·48	4·91
Phosphates,	$M^{ii}{}_3{}^2PO_4$	63·66	4·89

M represents a monad, M^{ii} a dyad, &c. The atomic heat is obtained by dividing the numbers given in the third column by the number of atoms entering into the composition of the compound.

The molecular heats of analogous compounds, as is seen in the table, approach one another closely. The carbonates and silicates ($M''CO_3$, and $M''SiO_3$), for instance, have the same molecular heat; so also with the chlorates and nitrates ($M'ClO_3$ and $M'NO_3$), the sulphates and chromates ($M''SO_4$ and $M''CrO_4$), the permanganates and perchlorates ($M'MnO_4$ and $MClO_4$), &c.

Specific Heat of Solutions.—When a salt is dissolved in water the water and salt retain the specific heat they had when separate. The specific heat of such a solution should then be represented by the formula:

$$Cp = \frac{100 + pk}{100 + p}$$

C = specific heat of solution, p = parts of salts in 100 parts of water, and k = specific heat of salt in separate state. But this formula is only approximately true.

A slight contraction attends the mixing of an aqueous solution with water, and the mixture has a molecular heat less than the sum of the molecular heats of the constituents. On the other hand a slight expansion accompanies the combination of potash or soda with hydrochloric, nitric, or sulphuric acids, and the molecular heat of the resulting compound is more than the sum of the molecular heats of its constituents. The reverse, however, occurs in the combination of these acids with ammonia (Thomsen.)

A certain relation is said to exist between the specific heats of mixtures, and the heat evolved in their formation. Thus Dupré states that the difference between the heat units evolved when given weights of two substances are mixed at t and at t′ is equal to the difference between the units of heat required to raise the mixture, and the separate constituents respectively, from the temperature t to t′.

Latent Heat.—When a body passes from the solid to the liquid, or from the liquid to the gaseous form, a certain definite amount of heat is absorbed by it, and rendered latent—that is, disappears as it were, and ceases for the time to affect the thermometer. This is called the *latent heat* of the body.

Latent heat may be defined to be "the quantity of heat which must be communicated to a body in a given state in order to convert it into another state without changing its temperature" (Maxwell). The change of state is accompanied by a change in the relative position of the molecules, or in their distance from one another; and this change must necessarily be attended with a destruction or production of the moving power on which the effects of heat depend. When bodies are heated and allowed to expand, the greater part of the heat is spent in communicating motion to the molecules of the body, but a part is used up in doing work against its molecular forces; and this is especially the case when a body changes its condition. Heat is thus employed when gases expand, as well as when solids are converted into liquids or liquids into gases. Latent heat has also been called *heat of fluidity*, inasmuch as it is regarded as the cause of fluidity in ponderable bodies.

The change which takes place when ice becomes water is to some extent gradual and not abrupt; hence the absorption of latent heat, so as to be complete, requires a certain range of temperature (Person). "Latent heat therefore simply resolves itself into an enormous increase of specific heat between certain narrow limits of temperature, and that in truth latent heat begins to be absorbed when

the specific heat begins to increase" (Stewart). This same doctrine of the gradual liquefaction of ice has been applied to account for the regelation of ice.

The doctrine of latent heat was first taught by Dr. Black, of Edinburgh. Since his time the subject has been carefully worked out by Watt, Rumford, Despretz, Southern, Provostaye and Desains, Clèment and Desormes, Regnault, Person, Andrews, Favre and Silbermann, &c.

Melting Point.—A solid body if gradually heated will melt and form a liquid. The temperature at which this *fusion* takes place is very different in different substances. Alcohol is liquid at —90°, mercury fuses at —40°, ice about 0°, many metals below a red heat, others not until raised to the highest attainable temperatures. Those bodies alone are infusible which decompose below their melting point (*e.g.*, wood).

The melting point of a body is constant under similar circumstances of pressure; and so long as any of it remains unmelted the temperature will not rise, the heat being given up to the unfused portion, which renders it latent. The freezing point generally coincides with the melting point; but it is possible to cool some liquid bodies several degrees below this point without solidification occurring. Water, for example, may be cooled below its freezing point if kept perfectly at rest, but a slight agitation suffices to cause it to solidify with a rise of temperature.

How to Estimate Latent Heat.—I. To measure the latent heat (x) of a body that is *liquid* at ordinary temperature, a known weight (w) is cooled below its point of fusion (R) to a temperature $-t$, and then plunged into a calorimeter containing water previously heated to a temperature (T) higher than the fusion point. The body rises in temperature till the melting point (R) is reached, absorbing $w\,c\,(t + \mathrm{R})$, c being the specific heat: next it melts and absorbs $w\,x$; at last an equilibrium of temperature is established (θ), and it thus gains $w\,c'\,(\theta - \mathrm{R})$, c' being the specific heat of the body in a liquid state. Taking W as the weight of the calorimeter valued as water, we obtain the formula $w\,c\,(t + \mathrm{R}) + w\,x + w\,c'\,(\theta - \mathrm{R}) = \mathrm{W}\,(\mathrm{T} - \theta)$, from which the value of x can readily be calculated.

II. In the case of bodies *solid* at ordinary temperatures we first liquefy the body and raise it to a temperature (t) much above its melting point, then plunge it into a calorimeter and accurately note the initial (T) and final temperature (θ). The calorimeter gains $\mathrm{W}\,(\theta - \mathrm{T})$; and the body loses 1st., $w\,c'\,(t - \mathrm{R})$ in cooling to its point of solidification (R); 2nd., its latent heat in solidifying, $w\,x$; and 3rd., $w\,c\,(\mathrm{R} - \theta)$ in cooling in the solid state from R to the final temperature, θ. The formula is:

$$w\,c'\,(t' - \mathrm{R}) + w\,x + w\,c\,(\mathrm{R} - \theta) = \mathrm{W}\,(\theta - \mathrm{T}).$$

III. The latent heat of a *vapour* is determined by distilling a known weight (w) of the liquid, the vapour, however, first having been passed through a serpentine tube surrounded by oil warmed to a temperature higher than the boiling point of the liquid. The vapour thus raised to a temperature T, is condensed in its passage through the coil in the calorimeter, and raises the temperature of the latter from t to θ. The vapour, 1st., loses $w\,c''\,(\mathrm{T} - \mathrm{R})$ in being cooled from T to its point of condensation, R, c'' being taken as the specific heat of the body in the state of vapour; 2nd., it liquefies and gives up $w\,x$; and 3rd., the liquid formed is cooled to the final temperature, and loses $w\,c'\,(\mathrm{R} - \theta)$. Therefore $w\,c''\,(\mathrm{T} - \mathrm{R}) + w\,x + w\,c'\,(\mathrm{R} - \theta) = \mathrm{W}\,(\theta - t)$.

Person's Formula for Latent Heat.—The latent heat (Z) may be expressed, according to Person, by the formula—

$$(160 + t)\,\delta = \mathrm{Z}.$$

160° C. is an experimental constant, furnished by researches on the latent heat of water; t is the melting point in centigrade degrees; $\delta = c - c'$, the difference between the specific heat of the body in its solid (c') and liquid state ($c°$). Take water as an example:—

$$t = 0°,\ \delta = (1 - \cdot 504) = \cdot 496.$$
$$\mathrm{Z} = (160 + 0°)\ \cdot 496 = 79 \cdot 36.$$

To obtain the latent heat of a body therefore, the difference of its two specific heats must be repeated as often as there are degrees between —160° and its melting point, from which it would appear that —160° C. is the absolute zero of heat. The value of δ is almost nothing with the metals; but Person is of opinion that if the metals could be retained in the liquid state below their ordinary melting points, δ would have a more considerable value.

TABLE OF LATENT HEATS OF LIQUIDS.

	Degrees C.	Degrees F.	Water = 1.
Water,	79 250	142·65	1·000
Sodic nitrate,	62·975	113·34	0·794
Potash,	47 371	85·27	0·598
Zinc,	28·130	50·63	0·355
Silver,	21·060	37·92	0·265
Tin,	14·252	25·65	0·179
Cadmium,	13·580	24·44	0·171
Bismuth,	12 640	22·75	0·159
Sulphur,	9·368	16·85	0·118
Lead,	5·370	9·65	0·067
Phosphorus	5·340	9·05	0·063
Mercury,	2·830	5·11	0·035

Disappearance of Heat in Formation of Vapour.—The latent heat of steam is much greater than that of water. So also with vapours generally; their latent heat is greater in the gaseous than in the liquid state—in other words, much more heat is absorbed by bodies in changing from the state of a liquid to that of a gas than in their liquefaction. Water exposed to a source of heat will rise in temperature until it begins to boil. If the source were uniform, the water would receive equal increments of heat in equal times. Provided the steam is allowed to escape freely, it will be found that the temperature cannot be raised above the boiling point, although the water still continues to receive as much heat as before. After this point has been reached, therefore, all the heat received is absorbed by the steam. The latent heat of steam can be recovered again by passing it through the worm of a

still; the water surrounding the worm is heated, and the steam returns to the liquid form.

Whenever a liquid evaporates without the application of heat, there is a depression of temperature produced. Water may easily be frozen by the cold resulting from its own evaporation, when this is made to occur rapidly, as under an exhausted receiver containing sulphuric acid, to absorb the vapour as soon as it is formed.

Any given substance absorbs the same quantity of heat to form gas or vapour of a given density, whether the evaporation takes place quickly *in vacuo*, or more slowly into a space previously filled with another gas; but the reduction of temperature is not so great in the latter case, as there is more time for heat to enter from without, and as the gas already present gives up a portion of its free heat.

The quantities of heat required for evaporation appear to be to one another nearly in the inverse ratio of the densities of the vapours produced, and accordingly more or less as the atomic weights of the substances; for if we multiply the latent heat of a vapour by its specific gravity, we obtain a series of numbers almost equal.

The cost in fuel in effecting the evaporation of different liquids is proportionate to the amount of latent heat in equal volumes of the vapours at their respective boiling points.

Measurement of Latent Heat of Steam.—Regnault determined the amount of heat that must be furnished to a pound of water at 0° C. in order to convert it wholly into saturated vapour at a given pressure. In this process there are two factors present: first, the heat required to raise the water from 0° C. to a certain temperature without evaporation; and second, the heat required to evaporate it entirely at that temperature and under the corresponding pressure. The water was boiled under high pressure, and the vapour formed was condensed almost as fast as it was given off. This saturated steam of given constant pressure and temperature was passed through the calorimeter, and condensed into water of a known temperature, in its condensation evolving its heat, and causing a measurable rise of temperature in the calorimeter.

Measurement of Latent Heat of Vapours.—The latent heat of a vapour may be determined by distilling over a known weight of the liquid, and condensing it in a large volume of water, the temperature of which is taken before and after the experiment. The method adopted by Andrews was as follows:—The liquid was boiled in a flask connected with a glass receiver that was attached to a spiral condensing tube, open at its free end. The receiver and its condensing tube were surrounded by a known weight of water, the temperature of which was accurately taken by a delicate thermometer before and after the experiment. When the liquid was boiled its vapour passed into the receiver, and was there in great part condensed. The weight of the liquid in the condenser being next carefully ascertained, and the necessary corrections made, the latent heat was determined by calculation.

Total Heat of Steam.—According to Watt, a given quantity of saturated vapour of any substance always contains the same total amount of heat, whatever may be its pressure, elasticity, or temperature. Part of this heat is latent and part sensible, and Watt concluded that the latent heat increases as the pressure on the vapour diminishes, and consequently as its temperature falls; while the sensible heat increases under inverse conditions. If this were true, equal weights of steam passed into cold water would have the same heating power whatever the temperature of the steam might be; and the same amount of heat would be required to evaporate a given weight of water *in vacuo* at a low temperature as under great pressure and at a high temperature.

According to Sothern, on the contrary, the latent heat remains constant at all temperatures. Regnault's researches, however, have shown both Watt and Sothern to be incorrect. He finds that when the unit weight of steam at t° is converted into water at the same temperature, and then cooled down to 0°, it gives out the quantity of heat (T) represented by the formula—

$$T = 606{\cdot}5 + 0{\cdot}305\,t.$$

The latent heat will be found by subtracting t from the value of T; or, as T is equal to L + t, substituting this for T, by the formula—

$$L = 606{\cdot}5 - 0{\cdot}695\,t.$$

The latent heat therefore increases as the sensible heat rises, but the decrease is less rapid than the rise in sensible heat; for the sum of the two heats increases by the constant 0°·305 for each degree of rise of temperature.

Regnault accordingly infers that if a pound of water at 0° C. be heated without evaporation to 100° C., and then entirely converted into steam at that temperature, the total quantity of heat required will be 637 units. This is what he calls the total heat of steam:—

TOTAL HEAT OF STEAM.

Temperature of Saturated Vapour.	Total Heat.	Temperature of Saturated Vapour.	Total Heat.
0°	605·5	70°	627·8
10°	609·5	80°	630·9
20°	612·6	90°	633·9
30°	615·7	100°	637·0
40°	618·7	150°	652·2
50°	621·7	200°	667·5
60°	624·8		

LATENT AND SENSIBLE HEATS AT DIFFERENT TEMPERATURES.

Pressure in Atmospheres.	Sensible Heat.	Latent Heat.	Sum of Latent and Sensible Heats.
	Degrees C.	Degrees C.	
0·006	0°	606·4	606·5
1·000	100°	537	637·0
2·000	120°·8	522·8	643·6
8·000	170°·8	488·0	658·8

There is accordingly little saving of fuel in performing evaporations at low temperatures.

LATENT HEAT OF VAPOURS—(ANDREWS, FAVRE AND SILBERMANN).

	Equal Weights.	Equal Volumes.
Water,	537·90	1000
Wood spirit,	263·70	872·9
Alcohol,	202·40	963·1
Fusel oil,	121·37	1104·7
Formic acid,	120·72	574·4
Methyl formiate,	117·10	726·6
" acetate,	110·20	843·5
Formic ether,	105·30	806·0
Acetic acid,	101·91	632·3
Ether,	90·45	692·3
Carbon disulphide,	86·67	681·4
Oil of lemons,	80·60	1125·6
Oil of turpentine,	74·00	1040·5
Oxalic ether,	72·72	1097·5
Amylic ether,	69·40	1134·0
Phosphorus chloride,	53·42	752·9
Ethyl iodide,	46·87	756·8
Methyl "	46·07	671·8
Bromine,	45·60	754·1
Iodine,	23·95	627·9

These numbers indicate the quantities of water in grams., the temperature of which would be raised 1° C. by the condensation of a gram. of the vapour of the liquid at the temperature of its boiling point. Thus the conversion of 1 gram. of steam at 100° C. into water at 100° C. will raise 536 grams. of water from 0° to 1° C.

STATES OF MATTER.—There are three states of matter—the solid, liquid, and gaseous. The mechanical properties of matter in these states are different, and in the passage of matter from one state to another, a definite amount of heat is disengaged or absorbed, the latent heat of Black. In solids the molecular structure is usually very permanent, so that a mass of pure gold or platinum will retain the same structure for an indefinite period of time. But this is not always the case. Crystals of sulphur obtained by fusion are when first prepared translucent, but in the course of a few days become opaque. No change of this kind occurs in crystals obtained from a solution of sulphur in bisulphide of carbon, which belong to a different system from those obtained by fusion. Iron, when subjected for a long time to strong vibrations, loses to some extent its fibrous character and becomes brittle, and brass wire in the course of years becomes slowly disintegrated. If a junction is made by fusing the ends of two tubes together, which are formed of slightly different kinds of glass, the union will often remain without a flaw for months, but sooner or later fissures will appear.

A body which recovers completely its form when the compressing force or stress to which it has been exposed is taken off, is said to be perfectly elastic, and some solids appear to fulfil this condition provided the stress is uniform in all directions (Maxwell). If the change of form under the same stress continues to increase with time we have the viscous state. By compressing a number of sheets of lead they may be forced to enter a narrow passage, and to accommodate themselves to its inequalities like a mass of heated gutta-percha. Metallic sodium may be forced at the common temperature of the atmosphere through a fine aperture, and obtained in the state of wire; and Matthiessen has shown that the brittle metal bismuth may be obtained in the form of long wires by a similar process, if the metal is heated till it becomes soft, but not perfectly liquid. Many of the metals have been shown by Sir W. Thomson to be viscous at common temperatures, and the same observation applies even to glass. When a solid in the form of a rod is exposed to traction by suspending a weight to the free end it increases in length, while at the same time it diminishes in thickness.

The solid is the only condition of matter capable of assuming the crystalline form. Crystals may be obtained either by the cooling of the liquid or vapour, or they may be deposited from a solvent. The ordinary solvents are such liquids as water, alcohol, or bisulphide of carbon; but in some cases boracic acid and other fluxes are used as solvents at high temperatures. Ebelmen succeeded by the last method in preparing crystals of spinelle, and of other siliceous minerals, some of which are found in nature, and others new to the mineral kingdom. If large and regular crystals are required from a body such as arsenious acid in a state of vapour, the glass surface on which they are deposited should be moderately heated.

The passage from the vitreous to the crystalline state is seen in the devitrification, or partial crystallization of glass, which usually begins from a number of different points, and ends in the formation of opaque spherules through the mass of the glass. In some cases the effect of heat on the molecular condition of solids is very remarkable. The yellow oxide of mercury, prepared from the chloride by precipitation, becomes red when heated, and recovers on cooling its yellow colour, while the ordinary red oxide is permanent at common temperatures. The red iodide of the same metal changes at a moderate heat into a mass of greenish-yellow crystals, which, on being allowed to cool, recover slowly their original red colour, but if pressed by a hard body the restoration of the colour from the change of molecular condition is instantaneous. When heated to a fixed temperature ordinary phosphorus is converted into the red variety, which is insoluble in bisulphide of carbon, and differs in its physical properties from ordinary phosphorus. Many solids again pass into the viscid state when heated. Sulphur exhibits this property in a remarkable manner, changing into a red viscid mass, which is so tenacious that it may be drawn into fine threads.

The elements carbon, boron, and silicon may be obtained in permanent allotropic conditions, in which their specific heats and other physical properties are widely different. Weber has recently shown that at high temperatures the specific heats of these allotropic forms become identical for the same element, and are in accordance with the law of Dulong and Petit, according to which the product of atomic weights by the specific heats of the elementary bodies in the solid form is a constant quantity.

Solids when heated increase in volume; but the

rate of expansion is different for different solids, and the co-efficient of dilatation usually increases with the temperature. Among the metals, platinum expands the least, and its rate of expansion is nearly the same as that of glass; and hence a junction almost permanent may be made by fusing a fine platinum wire into a glass tube. Senarmont has shown that in crystals not belonging to the regular system, the conductivity or conducting power for heat is not the same in all directions. In a slice of quartz cut at right angles to the axis of the prism, the conductivity will be the same from the centre to the circumference; but this will not be the case in a plate of quartz which has been cut parallel to the same axis. The fundamental experiment of Senarmont can be easily repeated with a slice of selenite covered with wax, and having a perforation in the centre for the introduction of a heated wire. The wax on melting forms a well-defined ellipse from the unequal transmission of the heat.

When solids are heated to a certain temperature depending on the body itself, they pass into the liquid state with the absorption of a definite amount of heat. In the case of many bodies, such as iron, glass, boracic acid, &c., this change is preceded by a well-marked viscid condition. In all bodies hitherto examined there is a change of volume in the conversion of the solid into the liquid, the liquid usually occupying a greater volume than the solid; but in some cases, as water, bismuth, and cast iron, a diminution of volume occurs in liquefaction. J. Thomson drew the important inference on theoretical grounds that the melting point of bodies which expand in liquefying is raised by pressure, while it is, on the other hand, lowered if the body contracts in liquefying. He calculated in the case of water that the freezing point would be reduced 0°·0076 C. for each atmosphere of additional pressure. This result was experimentally verified by Sir W. Thomson; and Bunsen has shown that paraffin and spermaceti, which expand in liquefying, have their melting points raised by pressure. The remarkable phenomenon of regelation, first discovered by Faraday, has been successfully explained by J. Thomson from the lowering of the freezing point of water by pressure. When two pieces of ice at the melting point are pressed together, the pressure causes melting to take place at the portions of the surface in contact. The temperature of liquefaction is lowered, while the water so formed escapes out of the way. Hence, as soon as the pressure diminishes, the two parts are frozen together at a temperature below 0°. On the same principle is explained the following beautiful experiment, which is due to J. Bottomley:—A fine metallic wire passing over a block of ice has a weight attached to it, so as to exert pressure upon the ice. The wire will gradually enter the ice, melting the surface on which it presses, while the water thus formed immediately freezes again behind the wire, so that the block remains a solid mass after having been traversed by the wire.

Water may be cooled several degrees below the freezing point without changing into ice, particularly if it is deprived of air, and inclosed in an exhausted hermetically sealed vessel. Other liquids, such as bromine and glacial acetic acid, exhibit this phenomenon, so that the same body may be preserved in a closed vessel for any length of time, within a certain range of temperature, either as a solid or a liquid.

The determination of the compressibility of liquids is a problem of great difficulty, involving for its complete solution some mechanical questions which are not definitely settled. Regnault has attempted to ascertain by experiment the absolute compressibility of mercury and water, his method of operating being founded on equations supplied by Lamé. For one atmosphere, the compressibility of mercury is 0·000003517, or $\frac{1}{284000}$th of the original volume; for water the corresponding number is 0·00004746, or $\frac{1}{21000}$th of the original volume. Within the limits of his experiments, Regnault has confirmed the observation, first made by Œrstedt, that the co-efficient of compressibility does not sensibly diminish for these liquids when the pressure augments. But liquids near the "critical temperature" differ greatly in compressibility from mercury or water. They yield much more to pressure than ordinary liquids, and the compressibility diminishes as the pressure increases. The average compressibility for one atmosphere of liquid carbonic acid between 55 and 125 atmospheres is 0·00133, or $\frac{1}{750}$th of the volume under 54 atmospheres; while from 125 to 220 atmospheres, the average compressibility for each atmosphere is 0·00071, or $\frac{1}{1400}$th of the volume under 125 atmospheres (Andrews).

As a general rule, liquids dilate when heated, the only exception yet known being water, which contracts when heated from 0° to 4°. The dilatation of liquids by heat augments with the temperature, but not according to any simple law. For this reason there is an error of nearly 0°·2 in the mercurial thermometer at temperatures midway between 0° and 100°. At higher temperatures the error arising from this cause amounts to several degrees, and requires to be carefully corrected. The absolute dilatation of a liquid by heat, that is, its change of volume, independent of the change of capacity of the containing vessel, can be determined by the method of Dulong and Petit, which depends essentially on the fact that the heights of two columns of liquid communicating below by a horizontal tube are inversely as the densities of the liquids. Hence, if two columns of the same liquid, at different temperatures, be compared, the absolute change of volume due to the difference of temperature will be obtained. Thilorier observed that the dilatation by heat of liquid carbonic acid is greater than that of the gases, and Drion has found that the co-efficient of dilatation of liquid sulphurous acid increases rapidly with the temperature, being for 1° C., 0·00173 at 0° and 0·00486 at 100°. In the case of certain homologous liquids, such as the methyl and ethyl alcohols, the co-efficient of dilatation is nearly the same, if the liquids are examined through corresponding ranges of temperature from their boiling points.

The remarkable experiments of Leidenfrost, in which water assumes a spheroidal form when projected upon a hot plate, and evaporates without entering into ebullition, has been extended by Boutigny, who has shown that all liquids under these conditions maintain a temperature a few degrees below their boiling points. He was thus led to the remarkable experiment of freezing water upon a red-hot plate. For this purpose liquid sulphurous acid is floated on a red-hot plate, and a few drops of water allowed to fall upon the floating liquid. To the success of this experiment it is essential that the plate should always maintain a high temperature, and it will be found rarely to fail if a thick platinum capsule is taken, and heated by a gas flame cautiously fed with oxygen gas. By substituting solid carbonic acid for sulphurous acid, Faraday succeeded in freezing mercury itself on a red-hot plate. Liquids floating and evaporating without ebullition on a heated plate are usually described as being in the spheroidal state. This term, however, when applied to water floating on a cushion of vapour over a hot plate, is apt to mislead. The water is not here in any peculiar state. It is simply water evaporating a few degrees below its boiling point while floating upon its own vapour, and all its properties, even those of capillarity, are the properties of ordinary water at 96°·5 C. The interesting phenomena exhibited under these conditions are due to other causes, and not to any new or peculiar state of the liquid itself (Andrews).

When liquids are raised to their boiling point they abruptly assume the condition of vapour, and at the same time the temperature of the liquid becomes stationary, and independent of the temperature of the source of heat by which the ebullition is maintained. If the air be completely expelled from water it may be raised to temperatures far above the ordinary boiling point without entering into ebullition. In ordinary evaporation we have the silent formation of vapour at the surface of a liquid, the temperature of which is no longer independent of the supply of heat furnished by the source. The vapours thus produced, whether by ebullition or evaporation, if heated apart from the liquids which furnish them, have the properties of gases; and we have now to consider what is the distinction between a gas and a vapour. This distinction has hitherto been founded on principles which are altogether arbitrary. Ether in a state of gas is called a vapour, while sulphurous acid in the same state is called a gas; yet they are both vapours, the one derived from a liquid boiling at 35°, the other from a liquid boiling at —10°. The distinction is thus determined by the trivial condition of the boiling point of the liquid under the ordinary pressure of the atmosphere, being higher or lower than the ordinary temperature of the atmosphere. Such a distinction may have some advantage for practical reference, but it has no scientific value. The critical point of temperature affords a criterion for distinguishing a vapour from a gas. Many of the properties of vapours depend on the gas and liquid being present in contact with one another, and this can only be at temperatures under the critical point. A vapour may accordingly be defined to be a gas at any temperature under its critical point. According to this definition, a vapour may by pressure alone be changed into a liquid, and may therefore exist in presence of its own liquid, while a gas cannot be liquefied by pressure; that is, so changed by pressure as to become a visible liquid, distinguished by a surface of demarcation from the gas. Carbonic acid will thus be a vapour below 31°, a gas above that temperature; ether, a vapour below 200°, a gas above that temperature (Andrews).

Gases are distinguished from liquids by the property of expanding so as to fill uniformly the whole space of any vessel in which they are contained. In the so-called perfect gaseous state, matter will obey implicitly the external forces which act upon it, the volume of the gas being always inversely as the forces externally applied. The characteristic property of this state is $\alpha = \alpha'$, where α is the coefficient of expansion by heat of the gas under constant pressure, and α' the coefficient of elastic force under constant volume. It has not been ascertained with certainty whether this condition of matter actually exists in nature, although in gases, which are at temperatures greatly above their critical points and at ordinary pressures, the deviations from it can only be discovered by the most exact experiments. In the ordinary gaseous state, as it occurs in nature, there are two distinct causes of internal disturbance which are directly opposed, and according to the nature of the gas, and the conditions of temperature and pressure, sometimes the one and sometimes the other preponderates. One of these disturbances is due to the action of internal forces tending to produce a diminution of volume; the other is due to molecular actions producing a resistance to change of volume other than that which occurs in a perfect gas. In the case of the permanent gases, or gases which have not hitherto been liquefied, the resistance to change of volume becomes predominant between 100 and 200 atmospheres, and at higher pressures this resistance steadily increases. The laws of Boyle and Gay-Lussac apply rigorously only to the (ideal) perfect gas, and are particular cases of more general laws applicable to the gaseous state as it occurs in nature. According to the law of Boyle or Mariotte, the volume of a gas at a constant temperature is inversely proportional to the pressure externally applied; according to the law of Gay-Lussac the dilatation of a gas for each degree of heat is a definite fraction of its volume at 0°, or more generally at the initial temperature, the pressure remaining constant; or the increase of elastic force for each degree is a definite fraction of the elastic force at the initial temperature, the volume of the gas being constant.

If, as already stated, we put α for the coefficient of dilatation of air for 1° under a constant pressure, and referred to a unit volume at 0° and 760 millimètres, we have $\alpha = 0{\cdot}003670$, according to the experiments of Regnault; and if we put α' for the corresponding coefficient of elastic force under

constant volume, we have $\alpha' = 0{\cdot}003675$, according to the same observer. These numbers in the case of a perfect gas would be identical with one another under all conditions of temperature and pressure. The results become much more complicated when the gases are examined under high pressures, at which the internal (attractive) forces come strongly into play. The subject has been recently examined with care in the case of carbonic acid (ANDREWS, Bakerian Lecture for 1876), and we proceed to give a short account of this investigation.

The values of α change greatly with the pressure (indicated by the air manometer) and temperature, as will be manifest from the following table:—

p.	α (0° — 7°·5).	α (0 — 64°).	α (64° — 100°)
20·10	0·00607	0·00553	0·00496
24·81	0·00700	0·00620	0·00543
31·06	0·00895	0·00743	0·00617
34·49	0·01097	0·00845	0·00657

The values of α are average coefficients for the ranges of temperature specified. In the above table the volume at 0° was taken as unit; in the next table the values of α are referred to the unit volume at 64°.

p.	α (64° — 100°).	p.	α (64° — 100°).
40·54	0·00460	106·9	0·01315
54·33	0·00553	145·5	0·01822
81·11	0·00803	223·0	0·00840

The value of α increases with the pressure till a very high pressure is attained, when it changes its direction and diminishes. The latter apparent anomaly depends upon the carbonic acid having, between 145 and 223 atmospheres, passed from the gaseous state proper to the intermediate conditions, which, as we shall presently see, establish a continuity between the gaseous and liquid states of matter.

Even more important on theoretical grounds is the investigation of the values of α', the coefficient of elastic force. From an observation of REGNAULT that the air and carbonic acid thermometers march sensibly together, it has been assumed by some writers that the value of α' will remain constant at different temperatures. The results of the experiments from which the following table has been constructed will show that this conclusion is erroneous:—

p.	α' (0 — 6·5°).	α' (0° — 64°).	α' (64° — 100°).
21·48	0·00537	0·00524	0·00497
25·87	0·00588	0·00573	0·00541
33·53	0·00734	0·00697	0·00633

As the general result of this investigation, it follows that in the ordinary gaseous state the law of GAY-LUSSAC does not hold good, either in the case of α or α', and that the dilatation by heat of a body in the ordinary gaseous state, whether measured by its expansion under constant pressure, or by the increase of elastic force under constant volume, is not a simple function of the initial volume or initial elastic force, but a complex function, changing with the temperature.

In the next table is given the change of volume of carbonic acid gas under high pressures and at different temperatures. In this table ε is the ratio of the observed volume of the carbonic acid, at the pressure p and temperature t, to its volume under one atmosphere at the same temperature, t.

p.	t = 6°·5. ε.	p.	t = 64°. ε.	p.	t = 100°. ε.
12·01	$\frac{1}{12{\cdot}95}$	17·60	$\frac{1}{18{\cdot}57}$	20·17	$\frac{1}{20{\cdot}98}$
14·68	$\frac{1}{16{\cdot}13}$	34·92	$\frac{1}{39{\cdot}08}$	31·06	$\frac{1}{33{\cdot}05}$
17·09	$\frac{1}{19{\cdot}12}$	54·33	$\frac{1}{65{\cdot}97}$	53·81	$\frac{1}{60{\cdot}30}$
24·81	$\frac{1}{29{\cdot}62}$	81·11	$\frac{1}{114{\cdot}0}$	80·25	$\frac{1}{96{\cdot}65}$
27·69	$\frac{1}{34{\cdot}03}$	106·88	$\frac{1}{185{\cdot}5}$	105 69	$\frac{1}{137{\cdot}6}$
31·06	$\frac{1}{39{\cdot}59}$	145·54	$\frac{1}{325\ 9}$	145·44	$\frac{1}{218{\cdot}0}$
34·49	$\frac{1}{45{\cdot}80}$	222·92	$\frac{1}{446{\cdot}4}$	223·57	$\frac{1}{379{\cdot}3}$

If we put $\rho = \varepsilon p$, and calculate the values of ρ from the above table, these values will be found to diminish, as the pressures increase, at every temperature, with the exception of the last observation at 64°, where the value of ρ is greater than at the preceding observation. This arises from the cause already referred to—namely, the passage of the carbonic acid to the liquid-volume condition.

If on any two isothermal curves, or curves showing the changes of volume of a gas by pressure at a given temperature, we designate those points where the values of ρ are equal, or $p\,v = p'\,v'$, homologues or homologous points; and if m be the ratio of the external pressures at homologous points, or

$$m = \frac{p}{p'}$$

it will be found that for any two isothermals the values of m are always the same. This is the characteristic property of the ordinary gaseous state.

It follows that in the case of a body in the ordinary gaseous state, if the relations of pressure and volume are known at any one temperature, the corresponding relations at any other temperature may be calculated from the observation of a single homologue at the second temperature. Thus, the whole relations of volume and pressure will be known from a set of primary observations at one temperature, and the determination of one homologue for each of the other temperatures.

The general form of the primary curve itself, or curve exhibiting the relations of pressure and volume, is deduced from the value of $\varepsilon\,(1 - \rho)$ being found to be constant for the same temperature. Hence we have for the equation of the ordinary gaseous state,

$$v\,(1 - p\,v) = c$$

(ANDREWS' Bakerian Lecture for 1876).

In 1822 Cagniard de la Tour discovered that liquids, such as ether, alcohol, or water, when heated in hermetically sealed tubes, become reduced apparently to vapour in a space from twice to four times the original volume of the liquid; and in the following year Faraday succeeded in liquefying by the aid of pressure alone chlorine and many other bodies known before only in the gaseous state. An extended set of experiments on the effects of pressure at different temperatures on carbonic acid has led to the proof of the continuity of the liquid and gaseous states. If carbonic acid be raised to the temperature of 30°·92, and exposed to gradually-increasing pressure, it will be found on slight increase of pressure to undergo a rapid but not abrupt diminution of volume, without actually liquefying when the pressure is raised to about 73 atmospheres. At lower temperatures the gas may be liquefied by pressure alone. This temperature of 30°·92 is "the critical point" for carbonic acid. At higher temperatures the fall is less but still perceptible, till a temperature of nearly 48° has been reached, when it can no longer be observed. The following is the manner in which the passage by continuity from the gaseous to the liquid state may be demonstrated:—Take a given volume of carbonic acid gas at 50° C., or at a higher temperature, and expose it to increasing pressure till 150 or 200 atmospheres have been reached. In this process its volume will steadily diminish as the pressure augments, and no abrupt diminution of volume will occur at any stage, nor will there be any liquid formed. When the full pressure has been applied, let the temperature be allowed to fall till the carbonic acid has been cooled to 0°, or any temperature below the critical point. During the whole of this operation no breach of continuity has occurred. It begins with a gas, and by a series of gradual changes, presenting nowhere any abrupt alteration of volume or sudden evolution of heat, it ends with a liquid. The closest observation fails to discover anywhere indications of a change of condition in the carbonic acid, or evidence at any stage of the process of part of it being in one physical state and part of it being in another.

If it be asked what is the condition of carbonic acid when it passes, at temperatures above the critical point, from the gaseous state down to the liquid volume, without giving evidence at any part of the process of liquefaction having taken place, the answer to the question is to be found in the close and intimate relations which subsist between the gaseous and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle, that the passage will nowhere present any interruption or breach of continuity. Under certain conditions of temperature and pressure carbonic acid gas finds itself in a state of instability, and suddenly passes, with the evolution of heat, and without the application of additional pressure, to the volume which by the continuous process can only be reached through a long and circuitous route. In the intermediate conditions through which carbonic acid passes in the latter case, it would be impossible to say whether it is in the gaseous or liquid state. These conditions are, in short, intermediate states which matter assumes in passing by a continuous path from the ordinary gaseous to the ordinary liquid state. These properties of carbonic acid are not peculiar to it, but are generally true of all bodies which can be obtained as gases and liquids (Andrews).

J. Thomson, while tracing the course of the boiling line of a liquid, and examining the corresponding boundary lines between liquid and solid and between gas and solid, has shown that the three curves representing these lines meet in one point, to which he has given the name of the "triple point." This point is near the ordinary freezing point, but is not identical with it. It is, in fact, the freezing point which corresponds to the pressure of the vapour of the body when freezing in presence only of its own vapour, and therefore under the pressure of that vapour. At the triple point, and at no other, can the three states of the same body, solid, liquid, and gaseous, exist in presence of each other.

All gases and many liquids when brought into contact, either directly or with the intervention of a porous plug, have the property of diffusing through each other, slowly in the case of liquids, rapidly in the case of gases. Graham has established the important law that the rate of diffusion of gases is in the inverse ratio of the square roots of their densities—a law which admits of easy explanation on the kinetic theory of the gases. Graham's results have been fully confirmed by the later experiments of Loschmidt. Graham has made an important distinction of bodies into colloids and crystalloids, and has shown that solutions of the former diffuse with great difficulty, while solutions of the latter diffuse with facility through porous diaphragms. He has taken advantage of this property to separate crystalloids from colloids when in the same solution, and has given to this process the name of "dialysis."

The kinetic theory of the gases, first proposed by Daniel Bernoulli in 1738, is founded on the assumption that the molecules of elastic fluids are in a state of rapid motion in all directions, and by their impact produce pressure on the sides of the containing vessel. Bernoulli showed that on this hypothesis the volume of a gas should be nearly in the inverse ratio of the compressing force, and that when a gas is heated the velocity of the molecules is increased, the square of their velocity being proportional to the pressure if the gas is not allowed to expand. In later times Joule calculated the velocity of the molecules, and Krönig showed that the law of the diffusion of gases admitted of easy explanation on the kinetic theory. The subject has of late years been developed with great ability by Clausius, Helmholtz, Maxwell, and others. In solid bodies, to use the words of Maxwell, a molecule, though in continual motion, never gets beyond a certain very small distance from its original position in the body; the path which it describes is confined within

a small region of space. In fluids, on the other hand, there is no such restriction to the excursions of a molecule. It is true that the molecule generally can travel but a small distance before its path is disturbed by an encounter with some other molecule; but after this encounter there is nothing which determines the molecule rather to return towards the place from whence it came, than to push its way into new regions. Hence in fluids the path of a molecule is not confined within a limited region, as in the case of solids, but may penetrate to any part of the space occupied by the fluid. A gaseous body is supposed to consist of molecules moving with great velocity. During the greater part of their course these molecules are not acted on by any sensible force, and therefore move as straight lines with uniform velocity. When two molecules come within a certain distance, a mutual action takes place between them, and each starts on a new path. In ordinary gases the free motion of a molecule takes up much more time than that occupied by an encounter; but as the density of the gas increases the free path diminishes, and in liquids no part of the course of a molecule can be spoken of as its free path.

HYDROCYANIC ACID—*Cyanhydric acid*, *Cyanide of hydrogen*, *Prussic acid*. *Acide prussique*, French; *Blausäure*, *Berlinerblausäure*, *Hydrocyansäure*, German; *Acidum hydrocyanicum* vel *Borussicum*, Latin; CNH = HCy.—This compound, which from its animal origin has also been named *zootic acid*, was first isolated by SCHEELE. DIESBACH and DIPPEL, in 1704, discovered Prussian blue. Forty-eight years afterwards MACQUER found that lime-water resolved this substance into calx of iron (ferric oxide) and a combustible colouring matter, which he could not separate, but which combined with potash, forming *phlogisticated potassa*—ferrocyanide of potassium. GUYTON MORVEAU concluded in 1772 that this principle had acid properties. In the year 1782 SCHEELE succeeded in preparing the aqueous solution of prussic acid. BERTHOLLET, in 1787, described it as consisting of carbon, hydrogen, and nitrogen. PROUST and ITTNER discovered several of its compounds, and the latter is said to have procured anhydrous hydrocyanic acid by the action of hydrochloric acid upon cyanide of mercury, but being unable to condense the vapour, he pronounced it to be a permanent gas. GAY-LUSSAC, however, in 1811, effected its liquefaction, determined the relative proportions of its ultimate elements, and led the way to the intimate knowledge and useful application of many of its compounds.

Hydrocyanic acid exists ready formed in the moister parts of many vegetable structures, and is generated in many others in which it was formerly supposed to pre-exist, by the processes which have been devised for its extraction.

The kernels of a large number of fruits, such as bitter almonds, peaches, cherries, apricots, plums, quinces, &c., the blossoms and tender leaves of the peach, sloe, and mountain ash, the leaves of the Portugal and cherry laurel, and many other plants belonging to the orders *Pomæ* and *Amygdaleæ*, when steeped in water for a considerable time and then distilled, yield hydrocyanic acid, together with oil of bitter almonds.

According to LIEBIG and WÖHLER the hydrocyanic acid is for the most part produced by the fermentative action of the emulsin, also present, upon the amygdalin, decomposing the latter into glucose, oil of bitter almonds, and hydrocyanic acid. All the plants which by distillation yield hydrocyanic acid and bitter almond oil (C_7H_6O) contain amygdalin ($C_{20}H_{27}NO_{11}3H_2O$). The effect of the fermentation is expressed thus:—

Amygdalin.		Water.		Oil of Bitter Almonds.		Hydrocyanic Acid.		Glucose.
$C_{20}H_{27}NO_{11}$	+	$2H_2O$	=	C_7H_6O	+	CNH	+	$2C_6H_{12}O_6$.

Pure hydrocyanic acid is a colourless liquid, which freezes at —15° C., forming feathery crystals, and boils at 26°·5 C. It is inflammable, and burns with a purple flame. Its specific gravity is 0·7058 at 7° C. and 0·6969 at 18° C. It is soluble in water in all proportions, forming a liquid lighter than water which manifests acid reaction with litmus. Its odour is that of bitter almonds. The vapour of the anhydrous or of the concentrated aqueous solution is intensely poisonous if inhaled; when largely diluted with air it produces spasmodic contraction of the fauces, but if moderately pure it kills instantly. A single drop of the anhydrous acid produces immediate death when swallowed. The dilute acid has a cooling effect on the tongue whilst in the mouth, but leaves a strong bitter after taste.

Exposed to the air, the anhydrous acid undergoes spontaneous decomposition, giving off ammonia and leaving a brown residue. The aqueous solution decomposes into ammonia and ammonium formate, particularly when exposed to light. The presence of a very small quantity of a mineral acid or a formate prevents this change, but addition of a large quantity promotes it, in this case formic acid and ammonia being set free:—$CNH + H_2O = CH_2O_2 + NH_3$. The ammonium formate when heated splits up into water and prussic acid thus:—

Ammonium Formate.		Hydrocyanic Acid.		Water.
NH_4CO_2H	=	CNH		H_2O.

Hydrocyanic acid is decomposed by the electric spark, by the voltaic current, or by passing it through a red-hot tube, into cyanogen (CN) and hydrogen, a small quantity of carbon and nitrogen being at the same time separated.

Hydrocyanic acid is produced in the dry distillation of many nitrogenous bodies, by the action of nitric acid on certain organic substances, by the decomposition of amygdalin, by the action of sulphuric or hydrochloric acid on cyanides, and by the decomposition of most of the cyanogen compounds and fulminates.

The London pharmacopœia Acidum Hydrocyanicum Dilutum contains 2 per cent. by weight of hydrocyanic acid. The instructions are:—Take of yellow prussiate of potash 2¼ ounces, sulphuric acid 1 fluid ounce, distilled water 30 fluid ounces or a

sufficiency. Dissolve the prussiate of potash in 10 ounces of the water, then add the sulphuric acid previously diluted with 4 ounces of the water, and cooled. Put the solution into a flask attached to the condenser and receiver of a distilling apparatus; and having put 8 ounces of distilled water into the receiver, and provided efficient means for keeping the condenser and receiver cold, apply heat to the flask until by slow distillation the liquid in the receiver is increased to 17 ounces. Add to this 3 ounces of distilled water, or as much as may be sufficient to bring the acid to such a strength that 100 grains of it, precipitated with a solution of nitrate of silver, shall yield 10 grains of dry cyanide of silver.

If a large quantity is to be made, great care must be bestowed on the close fitting of the distilling apparatus. The joints may be luted with a mixture in water of 1 part of almond meal and 5 parts of linseed meal brought to the consistence of putty. The retort is placed in a bath of chloride of calcium in water in an iron pot: 10 parts of yellow prussiate of potash mixed in a mortar, with dilute sulphuric acid, prepared by adding 6 parts of acid, spec. grav. 1·850, to 42 of water, are then poured into the retort, and the head luted on. A fire is then lit beneath the chloride of calcium bath, and the distillation proceeded with. The funnel into which the beck of the still dips should be covered with a wet bladder to prevent the escape of the poisonous vapour. The worm should be kept specially clean. To each Winchester quart of the distilled acid, it is customary to add one drop of sulphuric acid to insure its keeping.

The preparation of anhydrous hydrocyanic acid is exceedingly dangerous, from the great volatility of the acid and its highly poisonous character. The process should only be performed in winter, and with the help of a freezing mixture.

The best method is to dehydrate the aqueous acid by agitation with pulverized chloride of calcium, added in very small quantities to avoid development of heat, the vessel being to the same end surrounded with a freezing mixture. The mixture after a time separates into two layers, the lower consisting of aqueous chloride of calcium, the upper of hydrocyanic acid in a great measure freed from water. This latter is again treated with chloride of calcium until no action takes places between the two.

Another method is to pass the vapour of hydrocyanic acid over chloride of calcium in a series of U tubes, and thence into a vessel placed in a freezing mixture.

The mixture distilled may in this case be 10 parts of yellow prussiate with 7 of oil of vitriol, and 14 of water. The retort should be heated very cautiously to avoid the slightest risk of breakage, and the temperature of the vessels containing the chloride of calcium should not be allowed to be below 90° Fahr., in order to prevent the condensation of the acid elsewhere than in the freezing mixture. The escape of vapour from accidental fracture of the apparatus would be exceedingly likely to kill the bystanders.

Hydrocyanic acid is poisonous to vegetables as well as to animals. When the stems of plants possessing irritability are immersed in the acid, they lose this property. It prevents the milk of lactescent plants from leaving its cells, and deprives seeds of their germinating power.

Experiments have been made on animals generally, from the *mammalia* down to the *infusoria*, with hydrocyanic acid. The effects appear to have been similar in nearly every instance, the animals being convulsed, and losing sensation and voluntary motion.

It was first introduced into medicine about the year 1806 by the Italian practitioners, Borea, Brugnatelli, and Rasori. Its use in England was much furthered by the investigations of Drs. A. T. Thomson and Elliotson in 1820 and the subsequent year. It has been tried as a remedial agent in many affections of the pulmonary organs, in derangements of the nervous system, in hydrophobia, as an anodyne, and as an anthelmintic, with questionable success; but it is now employed only for alleviating disorders of the stomach, and as a lotion, and, in the state of vapour, in certain affections of the eyes.

When given in medicinal doses, cautiously increased, Dr. Pereira observed the following effects:—A bitter, but peculiar taste; increased secretion of saliva; irritation in the throat; frequently nausea; disordered and laborious respiration, sometimes quick, at others slow and deep; pain in the head, giddiness, obscured vision, and sleepiness.

When administered in poisonous doses of moderate quantity a remarkably bitter taste is experienced immediately after swallowing the acid; this is soon followed by a sensation of faintness and giddiness, with salivation, and is succeeded by tetanic convulsions and insensibility; the respiration is difficult and spasmodic; the odour of the acid may be recognized in the breath; the pupils are usually dilated, though sometimes contracted; the pulse is small and imperceptible. When recovery takes place it is usually very rapid, and the whole period of suffering seldom exceeds half an hour, though there have been exceptions, in which the symptoms have extended over several hours.

The principal antidotes in cases of poisoning by hydrocyanic acid are chlorine, ammonia, cold affusion, and artificial respiration, but the efficacy of all these methods is doubtful; and unhappily the action of the poison is so exceedingly rapid that they can seldom even be tried.

In cases of poisoning the presence of hydrocyanic acid is detected by acidulating the suspected liquid with tartaric acid, and distilling off the prussic acid at a low temperature. Caustic soda is then added to the distillate till the latter is distinctly alkaline, and a mixture of a ferrous and ferric salt is added (ferrous sulphate partially oxidized by exposure to the air answers very well), and then an excess of hydrochloric acid. If prussic acid is present Prussian blue is formed, and remains undissolved. A much more delicate test is the conversion of the acid by ammonium sulphide into sulphocyanide of ammonium, when an additional drop of a solution of

a ferric salt will, if the acid be present, produce a blood-red colour.

ICE.—*Glace*, French; *Eis*, German; *Glacies*, Latin. Frozen water.—In very many technical processes it is requisite to abstract heat and to reduce the temperature. The natural means of effecting this object is furnished by ice, which has of late years become an article of commerce. Prior to the year 1840, little or no ice was imported into this country; but about that time the Wenham Lake Ice Company was formed, for the purpose of bringing ice from a lake at some distance from Boston, U.S. Eventually it was found that ice could be obtained with greater advantage from Norway, and at the present time a vast quantity is annually imported from that country. The price in 1876 was at one time as low as 15*s.* per ton. It commonly varies, according to the seam, from 18*s.* to 40*s.* per ton. The price at which it is sold retail—£7 to £9 per ton—is a great bar to its use for domestic purposes.

The advantages accruing from the use of ice for various manufacturing processes, and the increased demand for it, naturally led to various means being devised for procuring it artificially; and as an offshoot from this, to the construction of refrigerating machines, which, though considerably lowering the temperature of water, did not go so far as to produce ice.

Cold is produced in various ways, the principal being by radiation into space, by the liquefaction of solids, by the vaporization of liquids, by the dilatation of gases, and by electricity.

The last method of producing cold has as yet been merely the subject of scientific experiment. PELTIER discovered, in experimenting with the thermo-electric pile, that cold was produced by a current passing from the bismuth to the antimony.

The cold produced by radiation has been used in the production of ice for centuries. In the upper provinces of India ice is obtained by exposing water in shallow porous vessels on clear dry nights. In Bengal, shallow pits are dug, which are partially filled with straw, and on the straw flat pans containing water are exposed to the clear firmament. The water is a powerful radiant, and sends off its heat copiously into space. The heat thus lost cannot be supplied from the earth, this source being cut off by the non-conducting straw. Before sunrise a cake of ice is formed in each vessel. The nights most favourable for the production of ice are those which are clearest and most serene, and in which very little dew appears after midnight. TYNDALL ("Heat as a Mode of Motion") points out that to produce the ice in abundance, the atmosphere must not only be clear, but it must be comparatively free from aqueous vapour. When the straw on which the pans are laid becomes wet it is necessary to change it for dry, not only because when wet it is rendered more compact and efficient as a conductor of heat, but also because the vapour rising from the wet straw, and overspreading the pans like a screen, would check the chill, and retard the congelation.

WELLS, in his essay on "Dew" in 1818, pointed out that this is an effect of chilling by radiation. The upper parts of the grass radiate their heat into regions of empty space, which consequently send no heat back in return; its lower parts, from the smallness of their conducting power, transmit little of the earth's heat to the upper parts, which at the same time receiving only a small quantity from the atmosphere and none from any other latent body, must remain colder than the air, and condense into dew its watery vapour if it be sufficiently abundant.

The various mixtures of salts known as freezing mixtures afford examples of cold produced by liquefaction of solids. If ice at 32° Fahr. is melted over a fire, as long as the smallest particle of solid water remains the temperature of the liquid does not rise above 32°, although during the whole time heat is being absorbed. Suppose now the melting takes place by admixture with any substance which will cause rapid liquefaction, it is evident the heat must be supplied from the extraneous objects, and a very considerable degree of cold will be produced.

WALKER arranged a long list of substances which by their rapid solution are enabled to act as frigorific mixtures. Thus with:—

	Thermometer Sinks Degrees Fahr.
Ammonium nitrate,..... 1 part. Water,..... 1 "	From + 50° to + 4°
Ammonium chloride,..... 5 parts. Potassium nitrate,..... 5 " Water,.....16 "	From + 50° to + 10°
Ammonium chloride,..... 5 parts. Potassium nitrate,..... 5 " Sodium sulphate,..... 8 " Water,.....16 "	From + 50° to + 4°
Sodium nitrate,..... 3 parts. Nitric acid, diluted,..... 2 "	From + 50° to — 3°
Ammonium nitrate,..... 1 part. Sodium carbonate,..... 1 " Water,..... 1 "	From + 50° to — 7°
Sodium phosphate,..... 9 parts. Nitric acid, diluted,..... 4 "	From + 50° to — 12°
Sodium sulphate,..... 8 parts. Hydrochloric acid,..... 9 "	From + 50° to — 0°
Sodium sulphate,..... 5 parts. Sulphuric acid, diluted,.... 4 "	From + 50° to + 3°
Sodium sulphate,..... 6 parts. Ammonium chloride,..... 4 " Potassium nitrate,..... 2 " Nitric acid, diluted,..... 4 "	From + 50° to — 10°
Sodium sulphate,..... 6 parts. Ammonium nitrate,..... 5 " Nitric acid, diluted,..... 4 "	From + 50° to — 40°
Snow or pounded ice,..... 2 parts. Sodium chloride,..... 1 "	to — 5°
Snow, or pounded ice,..... 5 parts. Sodium chloride,..... 2 " Ammonium chloride,..... 1 "	to — 12°
Snow, or pounded ice, ...24 parts. Sodium chloride,.....10 " Ammonium chloride,..... 5 " Potassium nitrate,..... 5 "	to — 18°
Snow, or pounded ice, ...12 parts. Sodium chloride,..... 5 " Ammonium nitrate, ... 5 "	to — 25°
Snow,..... 3 parts. Sulphuric acid, diluted,.... 2 "	From + 32° to — 23°
Snow,..... 8 parts. Hydrochloric acid,..... 5 "	From + 32° to — 27°
Snow,..... 7 parts. Nitric acid, diluted,..... 4 "	From + 32° to — 30°
Snow,..... 4 parts. Calcium chloride, ... 5 "	From + 32° to — 40°
Snow,..... 2 parts. Calcium chloride, crystallized,..... 3 "	From + 32° to — 50°
Snow,..... 3 parts. Potash,..... 4 "	From + 32° to — 51°

The reduction of temperature produced by these mixtures is entirely due to the absorption of heat accompanying the passage of the salts from the solid to the liquid state. Faraday obtained a very intense cold (about —166° Fahr.) by dissolving solid carbonic acid in sulphuric ether, and allowing the mixture to evaporate.

Dr. C. W. Siemens many years ago made use of a refrigerating mixture for the production of ice in connection with his principle of regeneration of heat. When crystals of chloride of calcium are dissolved in water, a considerable reduction in temperature—about 30° Fahr.—takes place. This is not sufficient to produce ice from water of 60° or 65° Fahr.; but Dr. Siemens made an arrangement by which the water to be cooled exchanged heat with the spent liquor, thus producing an accumulation of the effect in the centre of the machine. This machine worked well, and produced ice at a considerable rate; but the salt employed—chloride of calcium—is not a pleasant substance to deal with; it has to be re-evaporated and crystallized; and all this manipulation makes the process, in Dr. Siemens' judgment, far inferior to the purely mechanical methods which have since been adopted.

In India the vaporization of water is commonly used as a means of producing cold. Water is placed in a metal bottle, which is then wrapped in a wet cloth and swung in the sun. The current of heated air dissolves up the aqueous vapour with great rapidity, and so enhances the amount of evaporation that heat is abstracted from the contained water. The porous bottles and jars so much used in the tropics cool their liquid contents by the rapid evaporation of the moisture which permeates the substance of the jar. When hot dry winds prevail in the arid parts of India, houses are cooled by blowing air through a thick matting kept constantly wetted with water. The evaporation of the water cools down the air to an agreeable temperature, and the hotter the wind, the greater is its avidity for aqueous vapour, and the greater the refrigeration.

The dilatation of gas, or the vaporization of liquids, are by far the most economical means of procuring refrigeration, and one or other, or both of these, are employed in all the freezing machines now at work.

The work to be done in the artificial production of ice is very lucidly stated by Dr. B. H. Paul (*Quarterly Journal of Science*, vol. vi., and *Society of Arts Journal*, vol. xvii.).

The amounts of heat abstracted from water, or from steam in the liquefaction of ice, and from steam in the heating of water, are the amounts which determine the liquid and vaporous states of water, and they represent the expenditure of heat requisite for converting ice into the liquid state, and water into the state of vapour.

Now when a pound of ice is immersed in about three-quarters of a pound of boiling water the ice gradually melts, and at the same time the water will be cooled down to 32° Fahr. In this case the amount of heat absorbed, or expended in effecting the liquefaction of the ice, is about three-fourths that corresponding to the interval between 32° and 212° Fahr. Again, if steam at 212° Fahr. be forced into water at 32° Fahr. it is condensed, the temperature of the water rising gradually to 212° Fahr. If the weight of the water be now ascertained it will be found to have increased by one-fifth. The amount of heat liberated is therefore about five times as great as that corresponding to the difference of temperature between water at 32° Fahr. and water at 212° Fahr. In like manner if ice be mixed with steam at 212° Fahr., the ice will be liquefied and the steam condensed, the resulting water being one-eighth heavier than the ice, and having the temperature of 35°. Therefore the amount of heat liberated in the condensation of the steam is about eight times as great as that expended in the liquefaction of ice.

In order to express the quantities and relative amounts of heat concerned in producing these and similar effects, it is necessary to adopt some effect of heat as the standard of comparison. In this country the "unit" of heat is the quantity of heat required to raise the temperature of 1 lb. of water one degree of Fahrenheit's scale.

Water at 60° Fahr. contains an amount of heat greater than that contained in an equal quantity of ice at 32°, to the extent of 170·65 heat units for each pound; so that to convert water at 60° Fahr. into ice, it is necessary to abstract that amount of heat from it. Thus. to produce 1 ton of ice it would be necessary to abstract from the water 62,720 heat units = 2240 lbs. × 28 (*i.e.*, 60° — 32°), in order to reduce it to the freezing point of water.

But to convert the cooled water into ice it is necessary to effect a still further abstraction of the heat, which in the latent condition determines the liquidity of water. That heat amounts to 142·65 units for each pound of water, according to the most accurate determinations of Person; and consequently for a ton it would be 319,536 heat units = 2240 lbs. × 142·65 latent heat of water.

Hence the total quantity of heat to be abstracted from water at 60° Fahr. in order to produce 1 ton of ice is 382,256 heat units (= 319,536 + 62,720). This is a quantity of heat equivalent to the evaporation of about 3 cwts. of water at 60° Fahr., and is not more than about one-eightieth of the heat capable of being generated by 1 ton of coal.

Refrigeration, or the artificial production of ice, is therefore simply a manipulation of heat. In generating steam, heat is communicated to water. In refrigeration heat is abstracted from water, and in this process the water, which is cooled, corresponds to the fuel which is burnt in generating steam. Just in the same way that fuel in burning yields its heat to the substance vaporized, so does water in refrigeration yield its heat to some substance capable of receiving it.

The amount of heat absorbed by a body in changing its state may be abstracted and transferred to some other substance capable of undergoing a change, such as vaporization, which involves an expenditure of heat. 1 lb. of water in becoming steam absorbs 966·10 heat units (Regnault); ammonia in becom-

ing gas, 900·00 heat units per lb. (Favre and Silbermann); alcohol in becoming vapour, 364·30 heat units per lb. (Andrews); and ether, 162·80 heat units (Andrews).

Applying these data to the artificial production of ice, it is evident that for a given weight of these liquids their efficiency in abstracting heat will be in the same ratio as the amount of latent heat in their vapours, and that the quantities of each of the above substances which would have to be vaporized in order to produce one ton of ice, by abstracting from water 382,256 heat units, would be in the inverse ratio, as follows:—Water, 395·669 lbs.; liquid ammonia, 424·728 lbs.; alcohol, 1049·272 lbs.; ether, 2348·000 lbs.

The expansion of an incompressible gas is another mode of producing cold. When atmospheric air is expanded heat is absorbed at the rate of ·069, or about $\frac{1}{14}$th of a heat unit for each pound of air expanded to the extent of ·002035, or about $\frac{1}{490}$th of its volume at 32° Fahr. By compressing air an equal amount of heat is liberated in proportion to the degree of compression, and the temperature of the air is raised. If the compressed air be thus cooled to a low temperature, and afterwards allowed to expand, so as to overcome some pressure or resistance, a part of the heat which determines the temperature of the air is absorbed or rendered latent in effecting the expansion, and thus the temperature of the air is reduced proportionately to the degree of expansion. Thus, for instance, if 1 lb. of air at 60° Fahr. (= 13·093 cubic feet under normal atmospheric pressure) were compressed to 1·24 cubic feet, the quantity of liberated heat would amount to 32·44 heat units.

Then, since air requires ·169, or about one-sixth of a heat unit, to raise the temperature of 1 lb. 1° Fahr. when the volume remains constant, the heat liberated by the compression would produce rise of temperature amounting to 191°·98 Fahr., equal to 32·44 heat units, and the temperature of the air would become 251°·98 (= 60° + 191°·98). By cooling this compressed air to 32° Fahr. the quantity of heat abstracted would amount to 37·18 heat units per pound of air, and by expanding it then to say 4 cubic feet, heat would be rendered latent in this expansion, and it would amount to 7·56 heat units. This heat would be abstracted from that to which the temperature of the air (viz. 32° Fahr.) was due, and the air temperature would be thereby reduced to the extent of 1° for every 0·169 heat unit thus rendered latent by the expansion, which in the case here supposed would be to the extent of 44°·72, that is to —12°·72 Fahr.

Every pound of air cooled to this temperature would reduce the temperature of about ·108 ton of water 60° to 32° Fahr., so that to cool a ton of water from the higher to the lower temperature by this process, it would be requisite to compress and cool to 32° Fahr. 9·256 tons of air; and then to convert the cooled water into ice, it would be requisite to compress and cool a further 46·28 tons of air, or in all 55·53 tons of air to produce 1 ton of ice.

The mechanical production of cold by the air machine exemplifies the principle involved in refrigerating machines of all kinds. Every machine for producing cold by a continuous circle of mechanical operations, without the use of anything colder than the body it is desired to cool, is simply the negative solution of a motive-power heat engine (Alex. C. Kirk, "Inst. of Civil Engineers' Proc.," vol. xxxvii.). A motive-power heat engine absorbs heat at a high temperature, rejects it at a lower temperature, and developes an amount of power in proportion to the number of degrees through which the temperature falls. A machine producing cold is such an engine, absorbing heat at a low temperature, rejecting it at a higher temperature, and requiring work to be spent in driving it in proportion to the number of degrees through which the temperature is raised. Heat in falling from a high temperature to a lower temperature exerts "work," and "work" has to be expended to raise a low temperature to a higher temperature. The thermodynamic formulæ for every heat engine apply equally to the corresponding refrigerating machine; the work in the former appearing as a positive, and the latter as a negative quantity.

If the amount of heat rendered latent by vaporization of a substance were the only point to be considered in regard to its efficiency as a refrigerating agent, water would be the best material to employ for that purpose, both on account of the large amount of heat it requires for its conversion into vapour, and from its being more readily attainable than any other body with the exception of air. But it is also necessary to take into account the degree of facility with which the substances are vaporized, and the range of temperature within which they can be readily converted into vapour. The relation of ammonia, ether, alcohol, and water, in this respect, is shown in the following table, which gives their boiling points under the normal atmospheric pressure of 30 inches of mercury, and the tension of their vapours at different temperatures:—

		Ammonia. Boiling Point —28° 66.	Ether. Boiling Point 95°.	Alcohol. Boiling Point 172°·2.	Water. Boiling Point 212°.
	Fahr.	Inches.	Inches.	Inches.	Inches.
Tension of vapour in inches of mercury at—	104°	463·64	35·81	5·26	2·16
	68	254·61	67·06	1·75	0·68
	50	181·58	11·28	0·96	0·36
	32	124·52	7·22	0·50	0·18
	— 4	55·03	2·66	0·13	—
	— 40	20·81	—	—	—
	—108·76	9·45	—	—	—

It is evident from these data that the differences obtaining in this respect entirely alter the relation of the substances as refrigerating agents. In the case of water, which has the largest capability of absorbing heat in vaporizing, the normal boiling point is much too far above the freezing point to admit of its being applied for cooling purposes; while at temperatures much below the normal boiling point, the tension of its vapour, which is the measure of the capability of vaporization, is so small that the rate of vaporization would not be

sufficiently rapid to produce the refrigeration required in making ice. The characters of alcohol in this respect are but slightly more favourable than those of water.

In the case of ether, on the contrary, the normal boiling point is only 35° above the ordinary atmospheric temperature, and at temperatures below that point its vapour has a considerably greater tension than those of alcohol and water. Still, the tension of ether vapour, within the range of 60° to —4° Fahr., is too small to admit of its being used as a refrigerating agent without increasing its rate of vaporization by means of an air pump and evaporating *in vacuo*.

With liquid ammonia, however, the case is very different. This substance is gaseous within the ordinary range of atmospheric temperature under normal pressure; and it requires, at ordinary temperatures, a pressure of from 8 to 10 atmospheres (117 to 150 lbs. to the square inch) to maintain it in the liquid state. At the same time, the latent heat of ammonia approaches very nearly to that of water, and the tension of its vapour between 60° and —4° Fahr. is about 18 times as great as that of ether vapour. This, then, is a material possessing the qualifications necessary in a refrigerating agent in a very high degree. It is only necessary to reduce the pressure by which ammonia is retained in the liquid state in order to effect its vaporization, and thus to bring into play its capacity for absorbing heat from water, or from any other substance to be cooled.

For making ice the choice of a refrigerating agent at present lies between air, ether, and ammonia, though practical experiments have also been made with sulphurous acid, acetate of methyl, carbon disulphide, &c. (J. Gamgee). Machines for making ice will of course perform any lighter work, such as cooling liquids or air.

Refrigerating machines are now largely used in breweries, since fermentation goes on to the greatest advantage at temperatures not far removed from the freezing point. For preserving meat in hot climates, and in transporting it, artificial means of reducing the temperature are coming into use, and will be much more extensively employed as cheaper and more ready methods of ice-making are devised. In hot climates refrigeration is of very high importance in a sanitary point of view; and if the means were forthcoming, houses and places of resort would be no doubt refrigerated with the same care and regularity that they are now, when necessary, heated.

Greaves recently stated that a vast quantity of water is discharged into the sewers which has merely been used for cooling purposes, and which has acquired no contamination, but is simply elevated in temperature a few degrees. To his knowledge a sum of at least £10,000 was quite lately paid annually to the East London Water Company for water used for this purpose by sugar-makers. The process of boiling *in vacuo* has now been practised for about fifty years; but recently there has been a great endeavour to lower the temperature under which the process is conducted. Sugar is now boiled at a temperature as low as 110° Fahr.; and as a consequence becomes at once a strong, bright, crystalline substance, instead of being carried through the earlier stages of a heavy syrup, to be afterwards clarified and made into loaves. The modern process would not be applicable without the aid of the low temperature, and this low temperature is only obtained by working under a high vacuum, and with rapid condensation of the vapour produced.

In brewing and distilling also, large sums are annually expended for water only used in maintaining low temperatures, not only to condense the spirits and expedite the work, but to keep up the quality, flavour, and even soundness in many liquors.

As an aid to the power of the steam engine, increased ease and rapidity of condensation is much needed. For instance, the temperature of the whole sea in the Bay of Bengal is for months as high or even higher than that of the condensed water or hot well of a steam engine in northern climates; and in consequence, many a steamer that can run at a high velocity and make excellent passages across the North Atlantic, becomes a mere tub in tropical seas, not only through defect of vacuum, but by the unfair labour thrown upon a surcharged air pump lifting and forcing over crooked passages, and through the ship's side, streams for which the apertures were not adapted, and with strains for which the parts were not designed.

So far as the subject has been at present investigated, it appears that mechanical refrigeration may be obtained at a much cheaper rate if the reduction of temperature required be something less than from about 60° Fahr. to the freezing point of water. Thus, an air machine producing ice will work far less economically than one producing only cool air.

Orlick states that in Truman's brewery eighteen barrels of water, each weighing 360 lbs., were cooled 10° by using 4 cwts. of ice. Each pound of ice, in being converted into water of a final temperature of 51° Fahr., absorbed 161 heat units, and 4 cwts., or 448 lbs., × 161 = 72,300 units of heat absorbed. Eighteen barrels of water in cooling down 10° would give off but 58,800 units, showing a deficiency of 13,500 units, which must have been absorbed by the vessel containing the water, or by the cooling effects of the atmosphere. Truman's ice machine, made by Siebe, could produce 6 tons of ice in twenty-four hours, or 5 cwts. per hour; in other words, it could cool 22½ barrels of "liquor" per hour 10°, or 81,000 lbs. 1° per hour. Comparing this result with that obtained when the machine was employed merely to cool water to be used in the ordinary refrigerators, Mr. King, the engineer to Messrs. Truman, found that the machine was capable of reducing the temperature of 26 barrels of water hourly 23°·5, or 611 barrels 1°—*i.e.*, was capable of absorbing 219,960 units of heat per hour. This gave an efficiency of 2·8 times as much as when ice was first made.

In another instance, given by King to Paul, he found that Siebe's ice-making machine, when used

for refrigerating "liquor" with an atmospheric temperature of 62° Fahr., 1000 barrels of water were cooled to the extent of 15°, or from 57° to 42° Fahr., within twenty-four hours. This result expressed in heat units amounts to 5,400,000 = 1000 × 360 lbs. × 15 degrees.

The machine with which this result was achieved was capable of producing about 5 tons of ice in twenty-four hours, whereas the refrigeration effected was, in fact, equivalent to the production of no less than 14 tons of ice from water at 60° Fahr.

	Heat Units.		Tons.
Refrigeration obtained,..	5,400,000	=	14·126
Quantity of heat to be abstracted from water at 60° Fahr. in producing 1 ton of ice,	382,256		

In many cases where refrigeration is required it is by no means necessary to produce ice, and in fact the advantage to be gained by not doing so is obvious, when it is remembered that the work to be done in cooling water to the freezing point is only one-sixth of that requisite for converting it into ice, and that in making ice five-sixths of the work required has to be done under the greatest disadvantage, within a range of temperature below the freezing point.

For instance, in curing houses, breweries, sugar refineries, and many like industries, where the object is to keep down the temperature of large inclosed spaces, or to cool down large masses of liquid to the extent of 10° or 25°, a machine of given capacity is far more profitably employed, and will do a far greater amount of actual duty by direct refrigeration to the extent required, than by making ice and using that for the purpose of cooling.

Dr. B. H. Paul compares the relative efficacy of the refrigerating agents used in the air, ether, and ammonia machines, as follows:—To produce ice at the rate of 5 cwts. per ton from water at 60° Fahr. the refrigeration must amount to 95,564 heat units per hour, that being the quantity of heat contained in 5 cwts. of water at 60° Fahr. above the heat contained in 5 cwts. of ice, 560 lbs. + 170·65 = 95,564. In the case of a machine worked with ether, the hourly rate of vaporization must amount at least to 587 lbs., with liquid ammonia must be at least 106 lbs., while with an air machine it would be necessary to compress and cool at least 14 tons of air.

With an ether machine vaporization is maintained by means of a powerful air pump worked by a steam engine. In the air machine, also, the compression of the air requires the expenditure of considerable power. In the liquid ammonia machine, on the contrary, there is no such expenditure of power requisite, owing to the high tension of its vapour at low temperatures. But it is necessary to keep up a great pressure within the apparatus, in order to convert the ammonia into the liquid state; and there is consequently greater difficulty in preventing leakage from the working parts of the machine. The use of ether as a cooling agent is attended with great advantage in this respect, as there is no outward pressure in the refrigerator, and when sufficient condensation is applied, only a very slight outward pressure in other parts of the machine. This circumstance admits of the work being done without much loss of material.

David Thomson considers that this gives the ether machine a great advantage over the ammonia for hot climates, since even in this country it is requisite to work at the pressure of 160 to 170 lbs. to the square inch when making ice, and in hot countries 200 lbs. pressure is needed. With machines working at such high pressures it is almost impossible to keep them absolutely tight, hence ether machines are much to be preferred for cooling purposes in such conditions.

The most perfect of all methods as regards cleanliness and freedom from loss is the air machine. Atmospheric air is compressed to one half its bulk, or to one atmosphere above atmospheric pressure. The compressed air is allowed to cool in contact with water, either by external application or by injection, and to expand again in a working cylinder. The amount of heat that disappears in the second working cylinder is the exact measure of the refrigeration produced, an amount which can be easily calculated; whereas the power expended is the difference of force involved in compressing the air at a higher, and expanding it at a lower temperature.

In 1857 a machine of this description was invented by D. Gorrie. It did not, however, produce satisfactory results. The engine was a good one and the air pump was judiciously constructed; but the connection between the reservoir containing the compressed air, and the air expansion engine, was too narrow, and was provided with a throttle valve; there being evidently a vague idea in the mind of the inventor that the air would produce more refrigeration in expanding spontaneously without doing work than in expanding behind a working piston, an idea which was permissible at a time when the dynamical theory of heat was little understood.

Another defect was that the hot or compressed air was not sufficiently cooled before it was expanded, and was not deprived of its moisture. This latter was a great oversight, since the moisture in air plays a very considerable part in these machines.

At a temperature of 65° Fahr. saturated air contains 1 per. cent of vapour of water, and this has not only to be reduced into the liquid, but also into the solid condition, representing a total absorption of heat to the amount of 1140 units of heat per lb. of condensed vapour, which, upon the quantity of air, would represent 15° Fahr. of loss in the effect produced by expansion.

Since 1857 the air engine has been greatly improved by Kirk, Windhausen, and others. At a meeting in connection with the Vienna Exhibition, it was stated that a Windhausen machine of 150 horse-power produced 30 cwts. of ice per hour, the theoretical result being that that amount ought to be produced by 90 horse-power. The cost of producing a cwt. of ice by this machine was stated to be one shilling.

Kirk's air engine consists of a cylinder and a piston fitted with a wire-gauze regenerator, arranged in such a way that when the piston is moved the air inclosed in the cylinder may pass freely through the regenerator, and give out or absorb heat from it, the air being compressed at the one end of the cylinder, and thereby becoming heated, while it is expanded at the other end, and thereby becomes cooled. The heat generated during compression of the air is removed by a current of cold water circulating over the cover at one end of the cylinder, while the cooled expanded air abstracts heat from a current of brine circulating over the cover at the other end of the cylinder. During the time the displacing piston is moving up or down the air passes through the regenerator, which by retaining and giving out heat permits the passage of air without the passage of heat from one space to the other, however much the one may be colder or hotter than the other. Thus, when the machine is in action, the contained air is in a state of alternate compression and expansion. When the air is compressed in the lower space the heat generated is removed by the water flowing around it; and while the air is expanding in the upper space heat is abstracted from whatever solution has been placed in the upper part to be cooled. By the action of the regenerator, if it were perfect, the air would be returned to each chamber at the temperature at which it left it, and would commence both its heating and its cooling from that temperature. Thus, if no heat were abstracted at the lower end, and no heat supplied at the upper, the temperature of the lower end would continually rise, and that of the upper end continually fall, the power required to drive the machine continually increasing as the resistance to compression increased, and the assistance got from expansion diminished.

Practically there is a limit to this, since whatever be the material of the apparatus, ultimately such a difference of temperature between the hot and cold ends will be attained, that sufficient heat will be conducted through the piston and cylinder from the hot end to supply the heat absorbed at the cold end.

The efficiency of the regenerator increases nearly in proportion to the density of the air, but in a slower ratio; and it may be concluded that the efficiency of all other surfaces, such as the ends of the cylinder which give out or abstract heat from air, increases nearly as the density.

For a difference of temperature of 156° Fahr. between the hot and the cold sides of a regenerator, if it is clean and all the surfaces effective, it is not necessary to use more than fifty layers of gauze. This gives one layer of gauze for each 3° difference of temperature.

Only the surface exposed to the action of the air in a regenerator is of any value, the proportion of weight of material in a regenerator to weight of air passed through it being of no value.

The air contained in the machine may be at any pressure which the machine can withstand. At the Bathgate works of Messrs. Young, Meldrum, and Binney they are usually worked at from 100 lbs. to 120 lbs. per square inch maximum pressure, the efficiency and capacity of the machine for work increasing with increased pressure.

To keep up this pressure, a small compressing pump draws air through a couple of boxes containing chloride of calcium, two being used in order that they may be filled alternately with freshly fused chloride, and the air be drawn first through the one which has been longest in use, and next through the one freshly filled. This is necessary to dry the air; for if the air be damp the moisture is deposited as snow in the upper parts of the regenerator, and by obstructing the air passages does mischief.

As in spite of all precautions a little moisture will get in, the following arrangement has been made by A. C. Kirk to avoid the necessity of removing the regenerator and drying it at the fire. The eccentric rod of the machine can be disconnected, and thus all cooling action stopped although the compressing piston continues to work. By opening a valve, making communication between the upper or cold ends and the open air, and working the compressing piston, the air by its friction in rushing through soon warms the regenerator and evaporates the moisture from the interior.

By a machine thus constructed Kirk has succeeded in freezing mercury sufficiently to admit of its being hammered by a wooden mallet into a square bar before melting, the paraffin spirit in which the mercury was placed being at the same temperature a creamy slightly gelatinous substance. In so doing he maintained a difference in the apparatus of almost 100° Fahr.

A. H. Tait's compound pneumatic ice apparatus consists of two sets of pumps driven by steam or water-power; one set, No. 1, to compress sulphurous acid gas into fluid at a pressure of about 45 lbs. per square inch, or four atmospheres; and the other No. 2, to compress atmospheric air at a pressure of about 75 lbs. per square inch. To these are added two cylinders furnished inside with pipes, likewise designated Nos. 1 and 2, and an ice box in which the water to be frozen is congealed by a constant current of cold air which passes over and under the surface of the water in the vessel placed in the ice box.

Sulphurous acid may be economically made by forcing the products of the combustion of sulphur into an open vessel containing milk of lime or caustic soda, when the sulphurous acid will be retained in the form of calcium or sodium sulphite, while the nitrogen, carbonic acid, and undecomposed atmospheric air will pass off. The sulphite of lime in its fluid state is then placed in another air-tight wooden vessel, furnished with a vessel at the top to contain sulphuric acid, which can be let down as required into the solution, in order to set free the sulphurous acid, which is then passed through a clean vessel lined with lead containing sulphuric acid of 66° Beaumé, so as to deprive the gas of aqueous vapour, which would be detrimental in the process.

Sulphurous acid may also be made by sulphuric acid and scrap copper, sulphuric acid and char coal, &c.

The sulphurous acid set free by the action of the sulphuric acid on the sulphite of lime is passed to the pumps and compressing apparatus No. 1, by which it is forced into an upright cylinder filled with tubes of copper, coated outside with an alloy of tin and lead, the inside of the cylinder being lined with sheet lead. The gas is forced by the pumps No. 1 into the cylinder outside the tubes, and is there condensed at a pressure of about 45 lbs. per square inch, aided by a constant stream of cold water which surrounds the cylinder, and also passes through the pipes inside it. The liquefied gas is now let into another cylinder, No. 2, lined with lead inside, and fitted with copper pipes in the same manner as cylinder No. 1. The expansion of the gas in this cylinder cools the liquid circulating in the tube. After its expansion the gas is returned to the pumps to be again liquefied.

Liquid sulphurous acid boils at the temperature of 14° Fahr., or 18° below the freezing point of water; and if allowed to assume the gaseous form freely, it converts the fluid left behind into a solid, so great is the reduction of temperature. The inventor states that 1 ton of coal will produce 6 tons of ice.

The chief feature of the various ether and ammonia refrigerating machines which have from time to time been devised is the manner in which the vapour produced by evaporation has been gathered up and re-condensed, in order to serve over and over again. The method of reducing the temperature is the same as that which has been in use for centuries; the novelty consists in expending a certain amount of power in avoiding the loss of the refrigerating agent.

One of the earliest ice-machines used in this country employed ether, viz—that of Harrison in 1856.

This machine was subsequently improved by Siebe in 1862, *et seq.* In 1862 Kirk patented his air machine, which has done good work at the Bathgate Chemical Works, and also in breweries, &c. Reece's ammonia machine was patented in 1867. Since this date numerous other patents have been taken out, but all are more or less modifications of machines already existing, and no really new principle has been developed.

One of the earliest methods is the chemical one of producing refrigeration by evaporation in connection with absorption. Many vapours—ammonia being one of them—are readily absorbed by water, but can be separated again by the application of heat to the mixed liquid. A machine on this principle was shown by Carré at the Universal Exhibition, 1851, and very good results were arrived at with it.

It consisted of a boiler, which was filled with ammoniacal liquor, and the ammonia vapour was drawn off under considerable pressure into a surface condenser, composed of tubes surrounded by cool water. A separation was thus effected by heat of the ammonia from the water, and the ammonia, after being withdrawn into a vessel of lower pressure, evaporated at a very low temperature, and thus produced refrigeration, the vapours of ammonia being eagerly absorbed by water of ordinary temperature, forming mother liquor for re-evaporation in the boiler. This machine produces ice at the expense of about 1*s.* per cwt.

An ingenious modification of it for small applications on board ship, or for household use, has been devised. It consists of two vessels connected by a pipe, but hermetically sealed. One of the vessels contains the mother liquor, which is alternately heated and cooled, to drive off the ammonia, and to reabsorb it from the second vessel, which serves ultimately as condenser and refrigerator for the production of ice.

Reece's machine is an ingenious improvement on Carré's. In Carré's machine 100 lbs. of strong solution of ammonia, boiled by distillation to 5 per cent., yielded 75 per cent. of ammonia and 25 per cent. of water. This being condensed, was effectively used for refrigerating purposes. The only drawback was that the liquor condensed contained 25 per cent. of water, and holding a large quantity of ammonia, made the machine intermittent and relatively costly. The French Academy of Sciences appointed a commission to investigate the subject, and that commission pointed out that this was a bar to complete success in the machine, stating that what was required was a method by which ammonia could be had nearly anhydrous on one side, and an exhaust liquor on the other free from ammonia. This led Rees Reece to devise his machine. Two liquids having different boiling points can be separated when mixed by a process of fractionation. An ammoniacal solution treated in this way in his apparatus is divided, ammonia free from water being obtained on one side, and on the other water containing but little ammonia. The ammonia is passed into a condenser, and without the aid of machinery is compressed by its own force and liquefied. Passing the liquid ammonia into a refrigerator, connected with an absorbing vessel containing water or exhaust liquor, and simply opening a tap, the ammonia resumes its aëriform condition, and is dissolved by the liquor in the absorbing vessel.

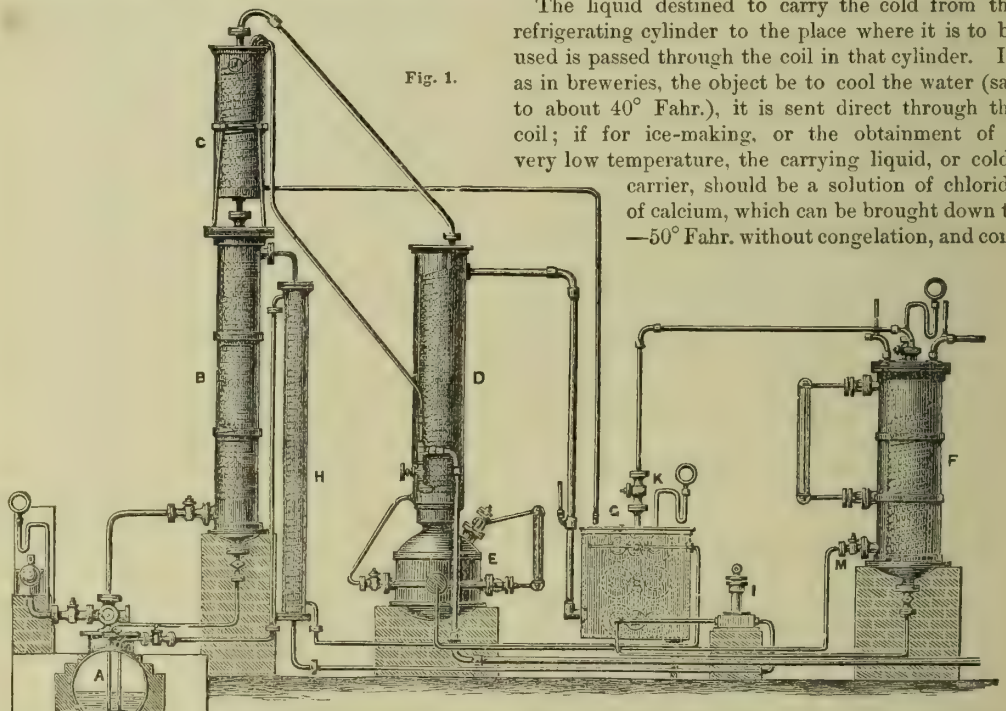
Fig. 1 illustrates Reece's apparatus. No motive power is required. The cold is produced by the alternate compression of ammonia gas into a liquid and its expansion into a gaseous form. The gas is driven off from its solution in water by the heat of an ordinary steam boiler, and the requisite compression of the gas is obtained simply by means of its own accumulation.

The apparatus consists essentially of two parts—one being employed in the distillation, rectification, and liquefaction of ammonia in a continuous operation. The second part is a refrigerating cylinder in which the anhydrous liquid ammonia, by the removal of pressure, is enabled to resume its aëriform condition, and passing forward to a properly-constructed absorbing vessel, is there redissolved by the exhaust liquor of the boiler, with which it comes in contact. It is thus used over and over again in a continuous manner and with but a minimum of waste.

In the engraving, A is a boiler or generator; B, the analyzing cylinder; C, the rectifier; D, the condenser or liquefier; E, store vessel; F, cooling cylinder; G, absorbing vessel; H, heater; and I, the ammonia pump.

The *modus operandi* is as follows:—The generator being charged with a solution of ammonia, a fire is lit beneath, and the air in the apparatus is driven out; a strong solution of ammonia is then pumped into the top of the analyzing cylinder, B, where, falling from plate to plate, it comes into contact with a current of steam from the boiler. The ammonia being thus separated in a great measure from the water, passes into the rectifier, C, where it is refrigerated by a current of cold water, and any aqueous vapour which may have ascended with it is removed. The ammonia, now become anhydrous, passes into the liquefier, D, when, the cock, M, being closed, it is liquefied by its own pressure. When a sufficient quantity has been liquefied, the cock, M, is opened, and the ammonia allowed to enter the cooling cylinder, F, until the coil is covered. Communication being now opened to the cylinder, F, by means of the cock, K, the liquid ammonia assumes its gaseous form, cooling the liquid contained in the coil of pipe in the cooling cylinder, F, as it passes. The ammonia thus exhausted passes to the absorbing vessel, G, where it is dissolved by the exhaust liquor from the boiler, A. This strong solution of ammonia is forced by the pump, I, through the heater, H (where it exchanges temperatures with the liquor coming from the boiler), into the top of the analyzing cylinder, B, where, falling through the plates, it is met by the ascending steam, and the process is repeated *ad infinitum*.

Fig. 1.



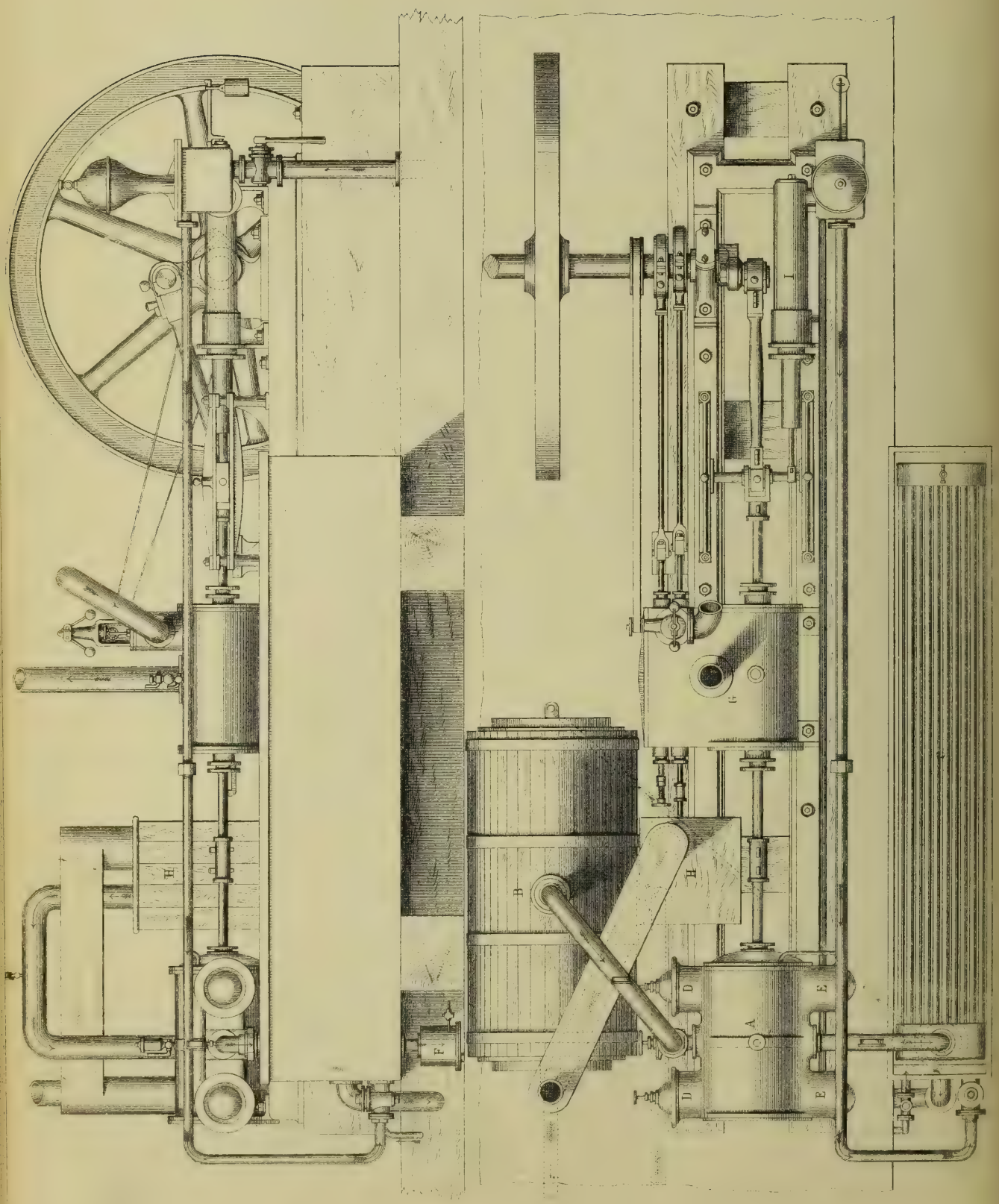
The liquid destined to carry the cold from the refrigerating cylinder to the place where it is to be used is passed through the coil in that cylinder. If, as in breweries, the object be to cool the water (say to about 40° Fahr.), it is sent direct through the coil; if for ice-making, or the obtainment of a very low temperature, the carrying liquid, or cold-carrier, should be a solution of chloride of calcium, which can be brought down to —50° Fahr. without congelation, and conveyed through pipes to any convenient place, and there used either to produce ice, to cool air, or in any other way; returning again in a continuous circuit to the refrigerating cylinder to take up a fresh store of cold.

The expense of working the process, as far as materials are concerned, is confined to the cost of the coal used in boiling a strong solution of ammonia and driving it forward to the condenser, within which it is rendered liquid by the pressure of its own accumulation without any other force being applied. The only motive power required is for working two small pumps, one of which feeds the analyzer with a solution of ammonia, whilst the other keeps the cold-carrying solution in movement.

The cost of artificial refrigeration by this process may be briefly stated thus:—For every 100 lbs. of coal required to work the apparatus, it will effect the cooling of 20,000 lbs. of water through 20° Fahr.—say from 65° to 45°; or it will reduce 1,000,000 cubic feet of air through 20°; or it will make 2000 lbs. of ice from water at 70° in an atmosphere of 80°.

In hot climates, houses or rooms may be cooled precisely in the converse way to their being heated in cold climates—the cold brine solution being passed through overhead pipes, instead of hot water or steam through underfoot pipes; or the holds of ships may be kept at a temperature low enough to admit of fresh meat being imported from the great cattle growing countries of Central Europe, Australia, or the River Plate.

Cost of making 50 tons of ice in twenty-four hours by Reece's machine, as stated by the inventor:—



J. B. LIPPINCOTT & CO. PHILADELPHIA.

2½ tons of coals, at 30*s.* per ton,	£3	15	0
50 tons of water,	0	10	0
Two men attending machine,	0	10	0
Waste of chemicals,	0	8	0
Wear and tear of plant,	1	7	0
Labour, weighing and removing ice from machine, at 2*s.* per ton,	5	0	0
	£11	10	0

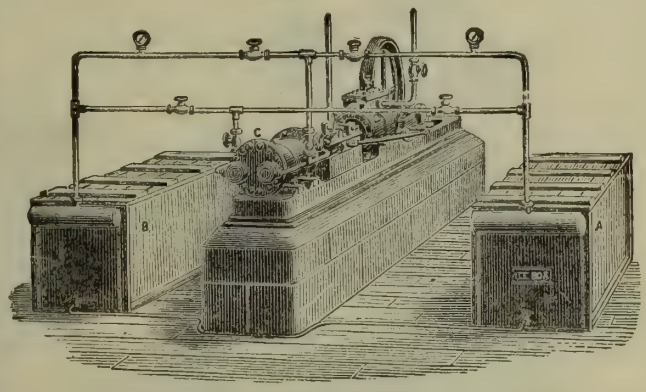
Equal to 4*s.* 7*d.* per ton of ice.

Fig. 2 represents Siebe Brothers' ice-making and refrigerating machine, designed for producing large blocks of ice in any desired thickness. The cost of manufacture varies from five to ten shillings per ton of ice, according to the size of the machine employed. The principle of this process of ice-making is the evaporation of a volatile liquid *in vacuo* (sulphuric ether is generally used), to produce cold, and the employment of the same liquid continuously without appreciable loss. The following is the action of the apparatus:—A vapour pump, C, is worked by the steam engine combined or separate, or any other motive power, as wind or water; the air pump maintaining a constant evaporation of the volatile liquid in a hermetically-closed chamber, filled with rows or series of tubes through which a current of salt water (used from its uncongealable nature) is passed; the cold therein produced cools the salt and water passing through the tubes, which is then circulated around vessels or ice moulds, A, containing the water to be frozen. After travelling thus, the brine is again returned to the refrigerator, B, or the chamber where refrigeration is going on, and passed through the tubes, where it becomes re-cooled, parting with the heat abstracted from the water in the ice moulds, and is conducted again around the moulds, until the water in the moulds is converted into solid ice. While the cooling of the brine, or "carrier of cold," is proceeding, the ether vapour drawn from the refrigerator by the vapour pump is then passed into a similar class of chamber, fitted with tubes, styled the condenser; these tubes are surrounded by water, and on entry of the ether vapour it is reduced to its liquid state again, and returned to the refrigerator for refrigeration. It will be seen from this description, that the process of ice making by this method is extremely simple and inexpensive. The same ether and brine being used over and over again, little or no expense is incurred further than the steam power for working the steam pump, and an attendant for the machine. We know from experience machines of Siebe's make have worked three months daily without a further supply than when first charged for starting.

Siebe's machines are now to be found in all parts of the world, and working for the past fifteen years are as good as when first erected. Numerous instances can be named where the introduction of one machine has led to the purchase of four or five more each successive season, as the profits are made from the last one put down. In confirmation of this, the manufacturers refer to Calcutta, Bombay, Delhi, Allahabad, Bengal, Colombo, Sourabaya, and many other cities and towns in the Tropics.

The application of these ice machines for cooling purposes, as used in breweries, oil refineries, and distilleries, has attracted special attention; and amongst the firms who have adopted them may be mentioned, Truman, Hanbury, & Co., Allsopp & Co., Guinness & Co., Murphy & Co., Beamish & Crawford, and almost all the breweries of any magnitude employ the machines for the purposes of cooling worts, cellars, tuns, &c. For the purpose of refrigeration the ice portion of the apparatus is removed, and the wort or water is passed through the tubes of the refrigerator, and so cooled. The application is not fixed to any quantity of liquor or wort, or to a fixed temperature. The machines will cool a small body of water to a very low temperature, or a larger quantity to a proportionately higher temperature; but as the worts in most breweries are not required very low in temperature the machines work at a moderately uniform rate.

Fig. 2.



Siddeley & Mackay's ether machine is shown in Ice, Plate I., where A is the vacuum pump; B, refrigerator; C, condenser; DD, suction valves; EE, discharge valves; G, steam cylinder; H, brine pump; I, cold water circulating pump; F, ether meter or ether regulator.

The ether liquid is placed in the refrigerator, B, where a vacuum is produced by means of the vacuum pump, A, and the vapour drawn over into the condenser, C (through which cold water is continually running), whence it returns through the ether regulator, F, into the refrigerator, B, this being constantly repeated at every stroke of the engine.

The cold produced in the refrigerator, B, by the evaporation of the ether, is absorbed by very dense salt water kept continually circulating by the brine pump, H. This brine is forced through the refrigerator, B, to the vessels containing the water to be frozen. Ice can be made in any shape or size.

For mercantile purposes ice is made in square blocks.

For the purpose of a skating rink the brine can be driven through a series of horizontal pipes, laid

on a non-conducting floor, and water placed over it.

The brine is kept circulating from the vessels containing the water to be frozen, or from the pipes of the skating rink to the refrigerator, and thence back again.

INDIA-RUBBER or CAOUTCHOUC, GUM ELASTIC.—*Caoutchouc, gomme elastique*, French; *Kautschuk, Amerikanisches Pfefferbaum harz, Federharz, Gummi elasticum*, German.—The concrete juice of several trees, mainly the *Siphonia elastica*, *Ficus elastica*, *Vahea gummifera*, *Hancornia speciosa*, and *Urceola elastica*. Of these the *Siphonia*, the *Ficus*, and the *Urceola* yield the greater quantity of the india-rubber of commerce. The *Siphonia* and the *Ficus* both belong to the sub-class *Monochlamydeæ*; but the former is placed by BENTLEY in the natural order *Moracæ*, while the latter is classed in the *Euphorbiaceæ*. The *Urceola* is by the same author placed in the natural order *Apocynaceæ*, sub-class *Corolliforæ*. The *Ficus elastica* and *Urceola elastica* are both normally natives of India; the *Siphonia elastica*, on the other hand, is a native of Brazil and Guiana. Since the first introduction of india-rubber, it has been found that several other trees, beside those from which the commercial substance is procured, yield a milky juice from which india-rubber can be produced.

The greater bulk of the india-rubber which finds its way into commerce is derived from a variety of sources, America, Asia, and Africa all sending their contributions. The exact localities from which the material, in greater or less quantity, is obtained, are as follows:—Para, Maranham, Pernambuco, French and English Guiana, Venezuela, New Granada, Peru, Panama, Costa Rica, Nicaragua, Salvador, the Antilles, Guatemala, Mexico, India, the Malay Archipelago, Borneo, Java, Penang, Gabon, Congo,

Fig. 1.



Fig. 2.



Angola, and Benguela. The variety of South American material known as Para, however, still maintains its ground as the best in the market. Of all the india-rubber-yielding trees, the best known is the *Ficus elastica*. Speaking of this tree WILLIAM GRIFFITH states that it is the vegetable monarch of the forests where it abounds, and that it may be recognized from a distance of many miles by the picturesque appearance of its dense and lofty crown. It grows either solitary or in groups of two or three together. The measurement of the trunk of the largest of a group gave a girth of no less than 74 feet, while the height was 100 feet, and the area covered by the extended branches was 610 feet. It was computed that over 43,000 of these trees grew within a length of 30 miles and a diameter of 8, in the forest near Ferozepore, in the district of Chardwar in Assam. The same tree has since been found by Lieutenant VEITCH to be equally plentiful in the district of Raudwar, and that in Assam its geographical range is between 25°·10 and 27°·10 north latitude, and between 90°·40 and 95°·30 east longitude. It flourishes on the slopes of hills up to an elevation of 22,500 feet. The engravings, Figs. 1 and 2, represent a branch of two of the principal india-rubber-bearing trees, viz., the *Siphonia elastica* and the *Ficus elastica*.

Historical Notice.—The first mention of caoutchouc appears to be in a work by HERRARA, who in speaking of the second voyage of CHRISTOPHER COLUMBUS, and with special reference to the natives of Hayti, describes a particular game of ball which was there in use, and in describing the balls he states that they were made from the gum of a tree, which from the tenor of the words used was undoubtedly india-rubber. With regard to an exact description of the leading characteristics of the tree which yielded the gum, JEAN TORQUEMADA appears to be the first author.

In his work, entitled "Monarquia Indiana," and published in 1615, TORQUEMADA describes a tree found in Mexico, and termed by the Indians "Ulequahil," and which he stated was held in great esteem. He then proceeds further to describe the general appearance of the tree, the method of procuring the juice, the characteristics of the gum itself (called by the natives "u li"), and finally, the uses to which the latter was applied, among which it is curious to find that it was in common use for making boots, and for rendering articles of apparel waterproof.

It is singular, and at the same time a proof of what is often lost by being ignorant of the literature of other countries, that although this description was given in the book mentioned as far back as the year 1615, the very existence of india-rubber appears to have been unknown to the civilized world generally until more than a century later. It was in 1736 that LA CONDAMINE described to the French Academy of Sciences his voyage to the Equator, and with special reference to Peru drew attention to a gummy material obtained by the natives of that locality, by incision from certain kinds of forest trees, called by them caout-chou, and which was used for a variety of useful and ornamental purposes. In 1761 FRESNEAU, who appears to have been previously acquainted with specimens of the material from Cayenne, investigated the Peruvian gum, and communicated his results to the Academy. MACQUER was the first who dissolved caoutchouc in ether, and constructed small tubes by the evaporation of the solution on moulds of the required form; he likewise comments on the extreme suitability of the material for various applications, in consequence of its elasticity and its indifference to the solvent action of the majority of ordinary liquids.

LA CONDAMINE very fully described the method of making bottles and other articles by means of appropriate clay moulds, dipping the clay into the liquid juice, giving it thus several coatings of material, and finally extracting the mould used by breaking or other means. He likewise mentioned the valuable application which india-rubber was capable of in the waterproofing of cloth. In the province of Esmaraldes the gum was called Hhévé by the natives, and was largely used for flambeaux, being wrapped between two leaves of the banana; these flambeaux were generally about 2 feet long and an inch and a half thick, and gave a brilliant light for twenty-four hours.

In England the use of caoutchouc was for some time confined to the erasure of lead pencil marks from paper, from which application it derived its familiar name of india-rubber. In the preface of a book by Dr. PRIESTLEY, published in the year 1770, and entitled "A Familiar Introduction to the Theory and Practise of Perspective," the following quotation occurs, "Since this work was printed off, I have seen a substance excellently adapted to the purpose of wiping from paper the marks of a black lead pencil. It must therefore be of singular use to those who practise drawing. It is sold by Mr. NAIRNE, mathematical instrument maker, opposite the Royal Exchange. He sells a cubical piece of about half-an-inch for 3s., and he says it will last several years." From the tenor of this passage, it would seem that at the time Dr. PRIESTLY'S work was published india-rubber was a comparative novelty in England, and it is noteworthy that even in the quotation to which attention has been drawn, the very name of the substance alluded to is not mentioned. HANCOCK likewise, in speaking of india-rubber, remarks that it was used for rubbing out pencil marks, that it fetched as high a price as a guinea an ounce, and that little was known of its history with the exception that it came from America. Soon after the practical introduction of india-rubber into commerce, great difficulties were experienced in dealing with the material in consequence of its altogether unique properties. A great advance in the mechanical manipulation was made by HANCOCK in the invention of what is now known as "the masticator," which enabled scrap rubber of all descriptions to be compounded into solid homogeneous masses, which could be afterwards used for the same purposes to which only good bottle rubber could be previously applied. The first masticator made by HANCOCK was only capable of taking a charge of 2 ounces of material, whereas the larger machines now in use are capable of dealing with as much as from 150 to 200 lbs. at a time. The function of the masticator was kept secret by HANCOCK for thirteen years, being called by the workmen "a pickle" in order to conceal its real use from the outside public. Other forms of masticators have been since introduced, the most important being that patented by NICHOLS in 1856, and differing mainly from HANCOCK'S original machine in possessing two rollers instead of only one. The invention of vulcanization by GOODYEAR and HANCOCK gave an immense impetus to the india-rubber industry, as it greatly multiplied the uses to which rubber could be applied. Vulcanization was patented in America by GOODYEAR, while the first English patent was obtained by HANCOCK in 1843.

Methods of Collecting and Coagulating the Juice. India-rubber is obtained from the different trees which furnish it by a method very similar to that employed for procuring gutta-percha. The trees, preferably those of mature growth, are tapped during the colder seasons of the year, the tapping being effected by making incisions in the bark round the trunk, commencing with the reflex roots, which generally lie exposed. The oldest trees are said to furnish the richest juice. The incisions are sometimes continued up the entire tree, the amount of sap which exudes increasing with the height at which the incisions are made, and the cutting is repeated once a fortnight or oftener during the gathering season. The milky juice which exudes is collected and treated in slightly different ways, according to the customs of the natives in each particular locality. In the original bottle india-rubber, in which form the first specimens of the material appeared in commerce in this country, the sap as it exuded was collected in suitable vessels, and moulds of clay were then plunged

into the liquid, removed, exposed for a short time to the heat and smoke of a fire to coagulate the layer of juice, redipped and reheated, until a sufficiently thick coating had been obtained (about half-an-inch or more). The whole was then plunged into water, and the clay softened and squeezed out, leaving a hollow flask of comparatively pure india-rubber. A second quality of material called "nigger's heads," was obtained by first procuring a comparatively thin coating of the gum on a clay mould in the way previously described, and then removing the clay mould, and filling the flasks or bottles so obtained with the remainder of the liquid sap, which was then coagulated and the excess of aqueous fluid expelled by exposure to heat or by being allowed to dry in the sun.

In Brazil the method of collecting the india-rubber by the natives from the *Siphonia elastica* is as follows. The trees begin yielding the material in sufficient quantity to repay the trouble of collection about the fifteenth to the twentieth year. Some ten or twenty incisions are made at once, and under each is placed a small receptacle for collecting the sap which exudes. A large bivalve shell is frequently employed for this purpose, being fixed to the tree by means of a lump of soft clay. The sap exudes drop by drop during from one to three hours, at the expiration of which period the sap has congealed to such an extent over the edges of each incision as to prevent the further flow of liquid. The shells used for collecting the sap have about the capacity of a small *liqueur* glass. Some three or four hours after the incisions have been made, the natives go from tree to tree emptying the contents of the shells as they pass into a sort of pail carried for the purpose. As the shells are emptied fresh incisions are made, so that a fresh quantity of sap is collecting while the liquid from the previous operation is being worked up. The pails are taken to huts where a fire is made, certain nuts found in the vicinity being thrown into the fire, to produce a smoke which is supposed to have a special virtue in helping the subsequent coagulation of the sap. Over the fire is placed a sort of large pipe of baked clay, the pipe being supported in such a way as not to retard the combustion. Flat wooden bats are next dipped into the vessels containing the sap, and then removed from the liquid and exposed to the heat and smoke of the fire, being rapidly turned about to prevent any over-heating or burning. In a little over a minute the coating of liquid sap has coagulated and become comparatively dry, when the instrument is again dipped in the liquid sap and re-exposed to the heated smoke, the operations of dipping and heating being alternately repeated some twenty times, when a sufficiently thick coating of india-rubber is obtained, weighing roughly about 4 lbs. Other bats are then coated in a similar way until the collection of liquid sap is exhausted. The edges of the masses of india-rubber are then slit, the wooden bat withdrawn, and the resulting flat pieces of rubber hung on cords or branches of trees to drain, when a blackish liquid drips from them. After the expiration of two or three days the material is ready to be sent into the market. The india-rubber thus prepared is termed in Brazil "seringa fina," and represents the first quality of material. An inferior quality is prepared from the pellicles of india-rubber which collect on the shells and on the edges of the incisions made in the trees; these are collected, the sticky fragments pressed together, moulded into rough balls, and exposed to heat and smoke as before, finally receiving one or two coatings of liquid sap.

At Nicaragua the fresh sap is said to be mixed with the juice of a species of vine, which has the singular property of causing rapid coagulation, and thus saving the time and trouble consequent on the alternate dippings and heatings practised by the natives of Brazil.

Physical and Chemical Properties of India-rubber.—Pure india-rubber prepared carefully from the fresh juice without exposure to smoke is nearly white, but the material as it occurs in commerce is generally more or less dark in colour. At ordinary temperatures it is supple, tenacious, and singularly elastic, permitting of being stretched very considerably without suffering any permanent elongation, and reassuming its original dimensions on being released from tension. If, however, thin threads of the material are stretched to seven or eight times their original length, and kept in this state of tension for a considerable time, they lose their elasticity, and remain at the length to which they have been extended. If the india-rubber in this condition is then exposed even momentarily to a gentle heat, the threads immediately contract to their original length, and regain their elasticity. This stretching is accompanied by a development of heat and increase in density, the specific gravity rising from ·9259 to ·9487, the material, however, reassuming its original density when its elasticity is restored by the application of heat. On being exposed to heat india-rubber becomes more and more pliant and soft, and at 170° to 200° C. it becomes semifluid, and of the consistency of treacle. After having once been heated to the temperature named it does not regain its original properties on cooling, but remains as a sticky, adhesive mass, which does not become to any degree dry, even after the lapse of several years. At a still more elevated temperature india-rubber decomposes and yields volatile hydrocarbons, analogous to those obtained when gutta-percha is exposed to similar conditions, viz, hevene, isoprene, and caoutchin. The distillate is an excellent solvent for india-rubber, but the price of its production has prevented its commercial utilization for this purpose; a patent, however, for its manufacture and subsequent use was secured by Barnard in 1833. By exposure to cold india-rubber loses its suppleness and elasticity, becoming at 0° C. hard, rigid, and inflexible; its original properties, however, are restored by the application of a moderate degree of heat. The specific gravity of pure india-rubber was found by Faraday to be ·925, and the density was not found to be permanently increased by exposure to heavy pressure. The density of the best Para rubber is said to be ·9415, that of Assam being ·9429, Singapore ·9366,

and Penang ·9192. India-rubber is totally insoluble in water, or in any of the ordinary aqueous solutions; it is not acted on by alkalies, alcohol, or dilute acids. Strong nitric or sulphuric acid, however, attack it in the same manner as gutta-percha; free chlorine also attacks it, converting it into a white brittle mass. The best solvents for india-rubber are coal-oil (coal-tar naphtha), turpentine, carbon disulphide, ether, and benzol; it is also dissolved by the fatty and volatile oils, and by melted naphthalin. The best solvent of all others is, according to GERARD, a mixture of 100 parts of carbon disulphide with 5 or 6 of absolute alcohol; the solution so obtained is stated to be as colourless as water.

The chemical constitution of india-rubber is identical with that of pure gutta, the hydrocarbon of gutta-percha. The percentage composition is as follows:—

Carbon,	87·5
Hydrogen,	12·5

India-rubber, in the form of the mechanically purified commercial article, is purer than similarly treated gutta-percha, in the sense of being unaccompanied by resinous oxidation products. There are, however, two varieties of rubber in commerce, in which have been identified small quantities of peculiar and characteristic substances. Gabon or Gaboon india-rubber, by treatment with ordinary alcohol, yields a crystallizable saccharine substance called Dambonite, the composition of which is represented by the formula $C_4H_8O_3$. This compound is white, easily soluble in water and in ordinary alcohol, melting at 190° C., and capable of being sublimed without decomposition by careful heating at from 200° to 210° in long, slender, shining needles. Borneo india-rubber yields a somewhat similar substance, to which the formula assigned is $C_7H_{14}O_6$. It is sweet, crystallizable, very soluble in water, but only dissolving sparingly in alcohol, melting at 175°, and subliming with slight decomposition at 205°.*

Ordinary india-rubber appears to be acted on in a somewhat curious way by ordinary solvents, the solution being in reality only partial. Placed in turpentine or in ether great swelling of the material first occurs, a turbid liquid being subsequently obtained, which appears to consist of a mixture of dissolved with suspended, disintegrated material. By the judicious use of solvents FARADAY was enabled to separate india-rubber into two distinct portions, each part, however, possessing very similar properties. Anhydrous ether was found to extract from amber-coloured india-rubber 66 per cent. of white, perfectly soluble matter, while oil of turpentine extracted from the ordinary commercial material 49 per cent. of a substance of a yellow colour. The solubility of different varieties of caoutchouc in benzol has recently been examined by HEEREN, and was found to be greatest in "Guayaquil" and "Para," and least in "Madagascar."

Although india-rubber in its ordinary condition is not subject to the comparatively rapid changes which attend the perishing of gutta-percha, it is found to undergo a slow alteration, when placed under certain conditions; namely, when under continued exposure to light it is subjected to extreme variations of humidity and dryness. A certain amount of oxidation then occurs, as will be seen from the experiments of MILLER (*Chemical Society Journal* [2], iii. 273)—A, representing the composition of the original material, and C, the composition of the portion dissolved by alcohol from A (11·8 per cent.) after it had been exposed to air and light for a period of nine months:—

	Carbon.	Hydrogen.	Oxygen.	Total.
A,	85·82	11·11	3·07	100
C,	67·23	9·54	23·23	100

Perhaps the most singular property of india-rubber is the change which it experiences when exposed to the action of sulphur at a high temperature, now known as "vulcanization" or "curing." The exact nature of the change which is produced by this process is at present very imperfectly understood, some thinking that the material simply experiences an allotropic modification, while others assert that the change is of a more essentially chemical nature. That a chemical action of some sort does actually occur during the curing process is obvious from the circumstance that sulphuretted hydrogen is invariably given off during the operation. In india-rubber vulcanized by immersion in melted sulphur, although about 15 to 20 per cent. of sulphur is absorbed, only a few hundredths really subsequently enter into combination, the rest being simply retained mechanically by the mass, and can be extracted by means of a suitable solvent. Vulcanized rubber containing an undue excess of free sulphur is apt to become brittle and to lose its elasticity after some time. With regard to the physical effects of vulcanization, they are exceedingly curious, the properties of the original material being singularly modified. While the untreated rubber becomes supple and comparatively useless on exposure to a moderate degree of heat, and hard and inflexible under the influence of cold, the vulcanized material retains all its properties unaffected under either of the conditions named. The elasticity of the rubber is at the same time very greatly increased, its porosity diminished, and it becomes unaffected by the solvents which attack the unvulcanized material. It also remains unaffected by grease and fatty oils, which render ordinary rubber supple and useless. The advantages secured by the curing process are thus very great, and have proved of immense value. There is another advantage which here deserves notice—namely, that the surface vulcanization which is adopted in the treatment of

* The natural juice of the india-rubber-bearing trees was examined by Dr. URE, and found to contain from 31 to 37 per cent. of the gum. The following analysis will give a general idea of the ordinary composition:—

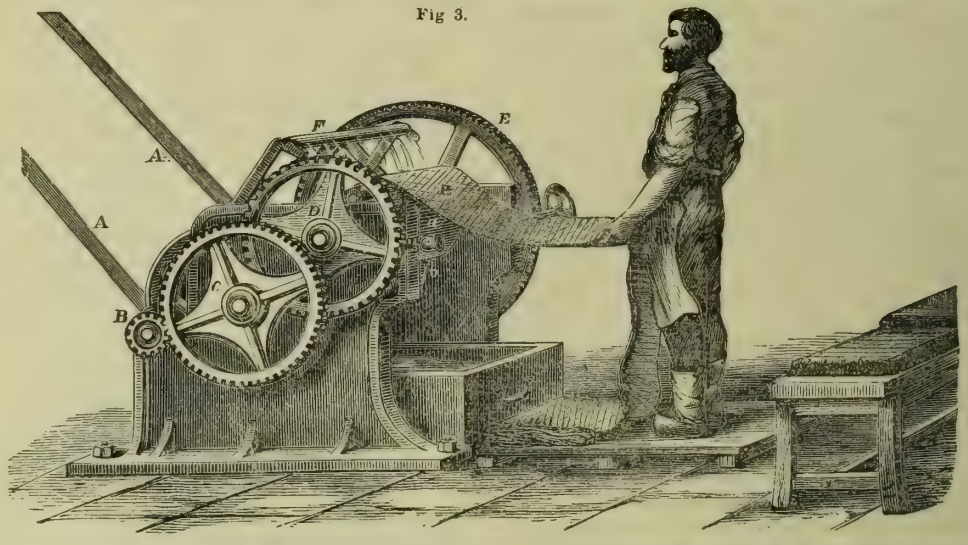
Water, containing a little free acid,	56·37
India-rubber,	31·70
Albumen,	1·90
Wax,	A trace.
A nitrogenous substance soluble in water,	7·13
A substance insoluble in water,	2·90
	100·00

Mackintosh goods entirely prevents the softening of the rubber on exposure to the solar rays, which was a very serious inconvenience experienced on the first introduction of these useful materials. With regard to the unchangeable nature of properly vulcanized rubber, the following interesting facts may be mentioned:—BROCKEDON placed a piece of vulcanized rubber in damp earth for a period of ten years, and found that at the expiration of that time its properties were unaltered. MACKINTOSH caused some logs of wood to be covered with vulcanized rubber, while others were left without any protective coating. Both were then towed in the wake of a vessel during her voyage to Demerara and her return to England. When the logs were subsequently examined, the coated specimens were found intact, while the others had become perfectly riddled by marine borers.

When the treatment of rubber is carried considerably beyond the degree of heat, duration of heating, and quantity of sulphur used in producing the ordinary elastic vulcanized material, a totally different substance is produced, termed vulcanite or ebonite. This material is generally black in colour, hard, of limited flexibility, and of about the consistence of horn. It is one of the best insulators of electricity known, and its property of becoming powerfully negatively electric by friction has led to its utilization for the plates of electric machines. It resists the action of solvents even more obstinately than the ordinary vulcanized material, scarcely even swelling when immersed in carbon disulphide. A curious fact in connection with ebonite is that the sulphur which it contains is oxidized by ozone, while ordinary free sulphur is unaffected by this agent. It is likewise a very expansible material, having three times the rate of expansion possessed by zinc.

India-rubber Manufacture — Purification of the Crude Material.—Rubber arrives in various forms

Fig 3.

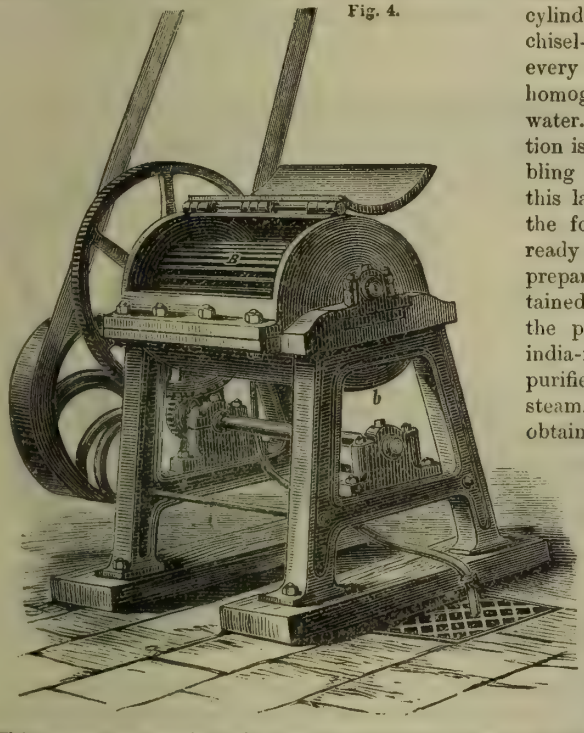


into commerce. The bottle variety of material is now only imported to a comparatively limited extent. The best Para rubber now arrives in the form of round or ovoid masses, weighing about 7 lbs. each; Borneo rubber occurs as square masses of about 10 lbs. in weight, while the African variety (Gabon) occurs generally in the form of balls, weighing considerably less. The treatment of the crude india-rubber in order to eliminate the various impurities with which it is associated varies somewhat at different places, but the following description will afford the reader a good insight into the general method of treatment:—The first step towards purification is to cut the crude article into small fragments, of a size which can be easily dealt with. These are then either introduced direct into a species of masticator (Fig. 3), or else subjected to a preliminary boiling in water, by which a great deal of the grosser impurities are removed. During the boiling, which is conducted in large vats or troughs, a constant stream of fresh water is allowed to flow in, in order that the washing process may be more complete. The water which flows off has acquired a most unpleasant smell from the impurity which it has acquired from the raw india-rubber. After the boiling process, the fragments of partly purified material are dried by being placed on plates of iron heated by means of steam. The fragments are kept continually stirred to facilitate the drying and to liberate any adhering dirt. After this washing and drying, the india-rubber is thrown between two cylinders which rotate with unequal velocity, a series of small jets of water falling at the same time upon the mass. The material is thus violently stretched by the rotation of the cylinder which has the most velocity, at the same time that it is pressed between the two cylinders and experiences a sort of rolling. This double movement causes a veritable tearing, which allows the water to carry away all foreign substances. The fragments of india-rubber are at length converted into a sort of rough crimpled sheet, which is repeatedly passed through the

apparatus, in order to eliminate all impurities and render the mass more uniform in character.

Fig. 3 represents the machine employed. B is a pinion in direct connection with the shaft, turned by the driving band, A A. This moves the large cylinder, C, which turns at a great speed; the extremity of this cylinder is seen at *b*. The cylinder, D, is turned at considerably less speed by a small cog-wheel attached to C (not visible in the drawing), and which plays into the teeth of the large wheel in connection with D. The pipe, F, pierced with small holes, supplies the small jets of water which play continually on the india-rubber. After having been treated as before mentioned, the sheet of india-rubber is dried, and subsequently placed in the "kneader" or masticator, where it is reduced to a homogeneous mass, and acquires greater density.

Fig. 4.



This apparatus consists of a strong cylindrical box, containing a stout iron drum, which is deeply fluted. Fig. 4 represents one form of this apparatus, where B is the fluted drum and A a pipe for the entrance of water, which flows eventually from the cylinder by an inferior orifice at *b*. In many cases a different form of masticator is used, in which two deeply-fluted rollers are used, which are made to revolve in opposite directions. The masticating process requires an immense expenditure of mechanical power, and the apparatus has to be made of very great strength. The actual size varies very greatly, but an ordinary masticator is about 3 or 4 feet long by about 1½ foot in diameter. The charge for this size of machine is about 20 lbs., the time of mastication being about three hours. The shaft upon which the internal drum is fixed has to be exceedingly strong, and is about 3 inches in diameter, the sides of the drum being 2 inches thick. Steam is admitted to the interior of the drum during the masticating process, and a current of water is kept circulating between the cylinder and its containing drum. One of the most curious features of this mastication is the great elevation of temperature suffered by the rubber during the process. The heat is such that if the water is admitted in too limited a quantity it is rapidly raised to the boiling point; and HANCOCK mentions that a lump of india-rubber which had been subjected to dry mastication indicated a temperature of 280° Fahr. when the mass was cut open and a thermometer inserted. After this combined kneading and washing, the material is subjected to a further kneading in the dry condition in an apparatus much resembling the masticator already described, with the exception that both the revolving cylinder and the case are armed with knives or blunt chisel-shaped teeth, which tear the india-rubber in every direction, and thus make the mass perfectly homogeneous and free from the last traces of air and water. The expulsion of the air during this operation is attended with a series of loud noises resembling small explosions. After being subjected to this last kneading, the india-rubber is obtained in the form of a compact solid mass, which is then ready for further treatment. In the old method of preparing sheet india-rubber, the sheets were obtained by direct cutting from a solid block; but at the present time nearly the whole of the sheet india-rubber is obtained by the passage of the purified material between powerful rollers heated by steam. In cutting sheet india-rubber the material obtained from the last operation was not sufficiently compact for the purpose; and for the double object of obtaining the desired degree of solidity, and at the same time preparing a block of sufficient size, a further kneading and mastication was performed in a larger machine than those used in the preceding operations, and at the end of this operation the mass of india-rubber was introduced into a rectangular cast-iron mould, where it was highly compressed by the action of a screw-press. When condensed to the utmost in this box, the lid was secured in its place by screw-bolts, and the mould set aside for several days. At the end of this time the masses of material were removed from the mould, and were then ready for being cut into any desired form.

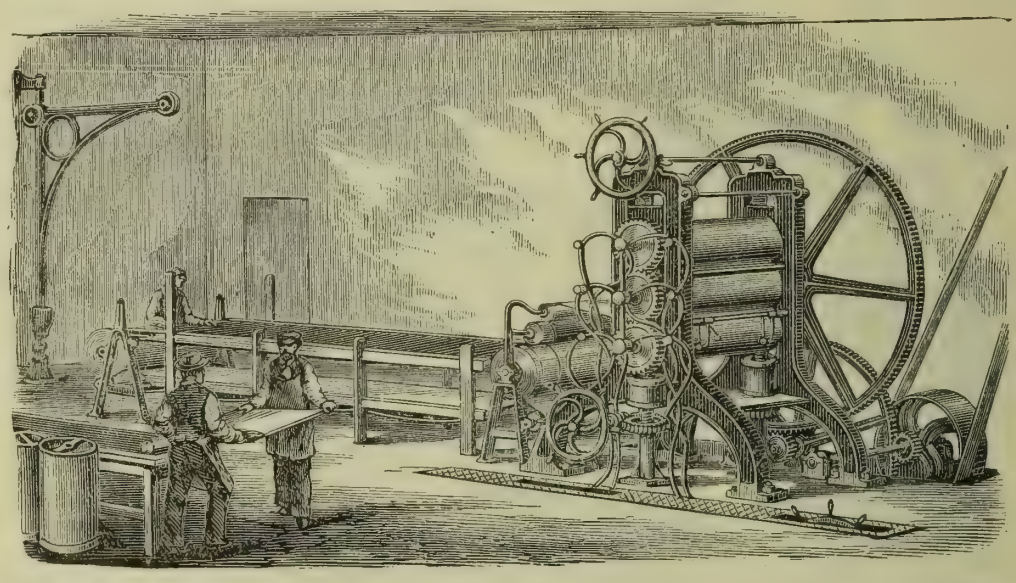
The method of preparing purified india-rubber is often not so elaborate as that described, and consists in softening and washing the crude material in hot water, reducing to small fragments, which are then subjected to the action of a machine resembling that shown in fig. 3, and the rough sheets then produced are finally subjected to a dry mastication for a sufficient time, to expel all traces of air and moisture and render the mass perfectly uniform and homogeneous. Sometimes a little quicklime is mingled with the india-rubber during the last mastication.

Preparation of Sheet India-rubber. — In the old

method of preparing sheet india-rubber by cutting slices from a previously prepared block, the mass of material was firmly secured in a machine, having a straight steel blade with its edges slanting downwards on to the surface of the block, which was raised regularly as the cutting progressed. By the horizontal vibrations of the blade the cake of india-rubber was rapidly cut into sheets of any desired thickness, from those sufficiently thin to cut into threads, to those destined to be subsequently recut into square or oblong blocks for the use of the draughtsman. During the cutting the knife as well as the surface being cut have to be kept continually wet by a stream of water.

We are informed by Foster and Williams of Bermondsey, the well-known rubber manufacturers, that the strongest sheet india-rubber is still obtained by cutting from solid blocks of the compressed material, the largest sheets thus made being about 8 feet long by 1 foot 6 inches in breadth. Much larger sheets, however, can be obtained by the passage of a block of purified material fresh from the masticator between highly polished steel rollers heated to about 200 Fahr. The sheets so obtained, however, are not so strong as those obtained from solid blocks by cutting. The rolling machines are called "calenders," and the distance between the rollers is regulated by an attached screw mechanism, so that by this means any thickness of sheet rubber can be produced. Sometimes the rolling is conducted on cloth, but this is not an invariable practice. The original rollers used weighed only about 2 or 3 cwts. each, whereas the weight of each now amounts to 3 or 4 tons, the whole machine being often as much as 50 tons in weight. The whole apparatus is represented at Fig. 5. The great advantage of the modern method of making sheet india-rubber lies not only in the comparative facility of production,

Fig. 5.



but likewise in the fact that the size of the sheets is not limited, as in the method of cutting from solid blocks. Fragments of purified india-rubber placed in the rolling mill (as it may be termed) unite with the greatest facility and produce perfect sheets, so that the material can be fed in continuously between the rollers, and the sheet produced wound off at the other end. From this sheet india-rubber all sorts of objects are fashioned, principally by hand, with the aid of the proper moulds and machinery.

Manufacture of Elastic Thread.—This is now a most important branch of industrial manufacture, carried on in London principally by Messrs. Warne of Tottenham, with whom it is quite a specialité, and also by the firm of Mackintosh & Co. India-rubber thread is very extensively used for making elastic fabrics, braces, garters, &c. One of the best descriptions of thread is a red vulcanized material prepared by Messrs. Warne by the aid of special machinery.

There are three methods of producing thread from india-rubber; the first two are strictly mechanical, while the third, although also in a sense mechanical, is of a totally different description, and is, we believe, not used at the present time. These methods are as follows:—

1. Cutting the material from sheets or bands by the action of a knife.

2. Obtaining the thread from sheets or bands by two or more knives working together, after the manner of scissors.

3. Manufacture of *round* thread by making the india-rubber into a paste by the addition of a limited quantity of a suitable solvent, and subsequently squeezing the paste thus produced through small orifices of the required diameter.

Of these three modes the second is that which is most used, but we shall now give a short description of each in rotation.

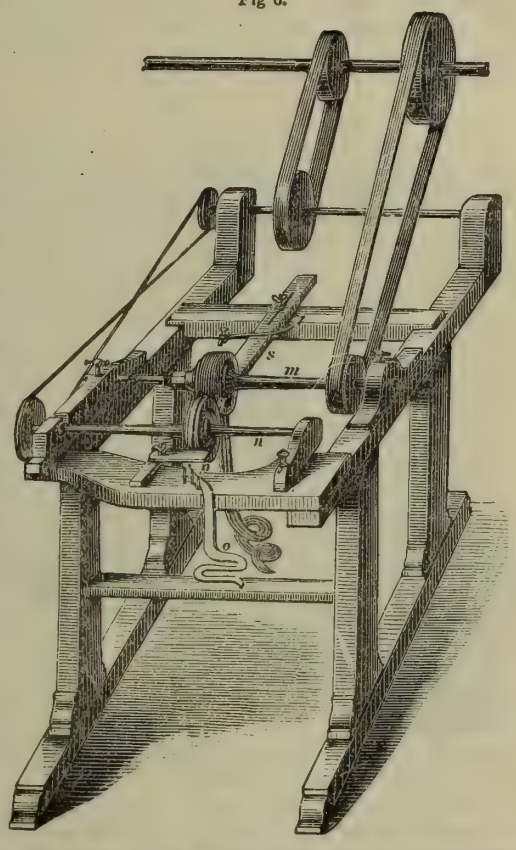
The commoner method of preparing thread by the first method is that of stretching a piece of india-rubber, having a tubular form and of the requisite thickness, over a mandril. This mandril is then secured to the shaft of a sort of lathe, which has one end formed into a fine threaded screw, that works in a fixed nut so as to traverse from right to left in its rotation. A shaft revolving parallel to the preceding carries a circular disc of steel, at such a distance as to cut through the india-rubber, so that by the transverse movement of the mandril shaft the hollow cylinder of material is cut spirally into a continuous fillet, the breadth of which is regulated by the pitch of the screw, and the rapidity with which the mandril shaft is turned.

The second method of manufacture is generally accomplished by first cutting the sheet rubber into narrow bands, of a breadth equitably proportioned to the number of threads into which each is eventually to be cut. These bands may likewise be produced from flat solid cakes of a circular shape, and having the desired thickness: the circumference of the cakes being advanced against a circular disc of steel having a sharp edge. By an automatic movement the centre of the india-rubber disc is made to advance upon the knife at such a regulated rate as to preserve the riband of equal thickness throughout the entire cutting.

Whether the bands are produced from sheet rubber or from solid cakes of india-rubber, they are eventually converted into thread either by a series of circular knives placed upon a shaft, or by a machine similar to that shown in the article Gutta-Percha, and used by Hancock for preparing threads or cords of the last named material. The circular steel knives employed by MM. Rattier and Guibal were set upon a revolving shaft, and separated from each other at the required distance by interposed washers. These knives acted against a series of others placed on a parallel adjoining shaft, and the band of india-rubber on its passage through the apparatus was simultaneously divided into eight or more threads. Nickels has patented a modification of this apparatus which is figured and described in his patent taken out in October, 1836. This form of machine is shown at Fig. 6. Various sizes of elastic threads are now manufactured, and are known by certain numbers which indicate the number of cuts to the inch.

The third mode of preparing thread, differing from those previously described, not only in being *round* in place of square, as is the case with cut thread, but likewise in the mode of preparation, was patented some time back by MM. Gerard and Aubert, and employed by them for some time at their manufactory at Grenelle, near Paris. In this process the india-rubber is first purified by the ordinary methods, and rolled into thin sheets, which are then cut into strips and introduced by hand into zinc boxes with wide openings; over the india-rubber is poured some carbon disulphide or benzol, containing about 5 per cent. of alcohol. The proper quantity of this solvent to use is about double the weight of the india-rubber, the exact amount being regulated by the quality of the gum. This being done, the lid of the box is adjusted, fitting into a very deep groove, packed with tow impregnated with a mixture of glue and treacle, or some other soft humid substance capable of resisting the action of the carbon disulphide vapour. After standing for from twelve to fifteen hours the india-rubber has become completely softened, and it is then in this condition introduced into vertical cylinders, the lower ends of which are fitted with wire-gauze. These cylinders are fitted with pistons, to which pressure is applied, and the pasty material is thus forced through the wire-gauze, and thus strained

Fig 6.

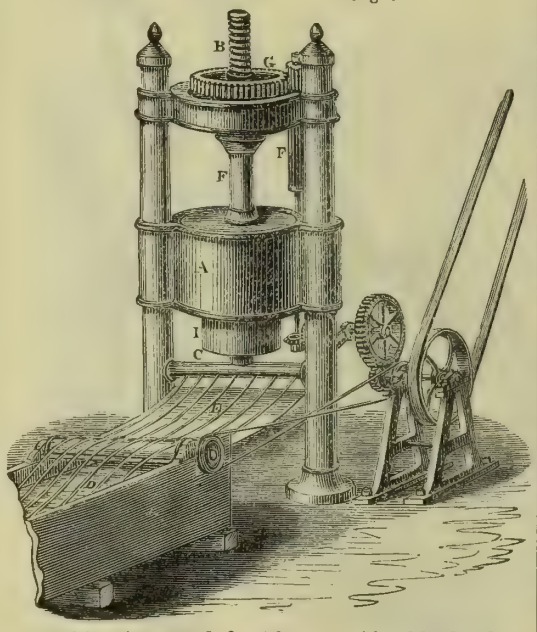


and mixed. The india-rubber paste is then introduced into the apparatus shown at Fig. 7, which consists of a cylinder, A, into which the material is introduced, in connection with which is the pipe, C, pierced with holes of the requisite diameter. The cylinder, A, is provided with a lightly fitting piston, F, which is capable of being worked slowly down by the screw, B. The pasty material is thus forced through the small orifices in C, in the form of round threads, which pass over a velvet band, E, into a tank of running water, D, from which they pass to a band of cloth about 600 feet long. After having traversed this band, which occupies about six minutes, the solvent is in great measure evaporated, and the threads have become comparatively dry. They are

then wound on to bobbins, and are dried for several days.

In weaving elastic threads or covering them with cotton or silk, the first proceeding is to deprive them of their elasticity. This is accomplished by stretching the threads to about eight times their original length, and then winding them in the strained condition on to the bobbins eventually used in the manufacture. After being left in this condition in a cold situation for some days, the exact duration necessary depending on the quality and character of the material, the threads have quite lost their elasticity; but this can at any time be restored by the application of heat, the threads at the same time contracting to their original length. The operation of stretching is performed chiefly by boys and girls, known as *tenters*, who press the thread between the thumb and forefinger, previously moistened with water. The

Fig. 7



stretching is attended with a considerable development of heat, so much so in fact as to be extremely unpleasant to unseasoned fingers. The india-rubber in stretching experiences a considerable contraction in volume, its density being at the same time considerably increased. Should the thread break it can be easily reunited by pressing the clean cut edges together. After the cloth is woven in the ordinary way, the elasticity of the india-rubber is restored by passing the fabric under a heated roller having a temperature of about 63° C. In the employment of *vulcanized* india-rubber for the manufacture of elastic fabrics, provision has to be made for keeping the threads stretched during the weaving process.

The chief seats of the elastic thread manufacture in England are Leicester, Derby, and Manchester, in many of which several hundred hands are daily employed.

India-rubber Tubing.—This branch of the india-rubber industry is gaining yearly in magnitude and importance. Tubes of ordinary rubber are made from sheet-rubber by a very simple process, consisting in wrapping a band of the material round a mandril, cutting the two edges, and pressing them firmly and rapidly together, when a perfect union is effected. The operation may be performed automatically by suitable machinery. Tubing can also be made from india-rubber paste, prepared in the same way as that used by Gerard and Aubert for the preparation of round thread. The machine used for the manufacture of tubing by this method is exactly similar to that employed for preparing tubes of gutta-percha (see article Gutta-Percha). The greater quantity of the india-rubber tubing of commerce, however, is made of the vulcanized material, and in this case india-rubber cement is used in order to insure a stronger joint.

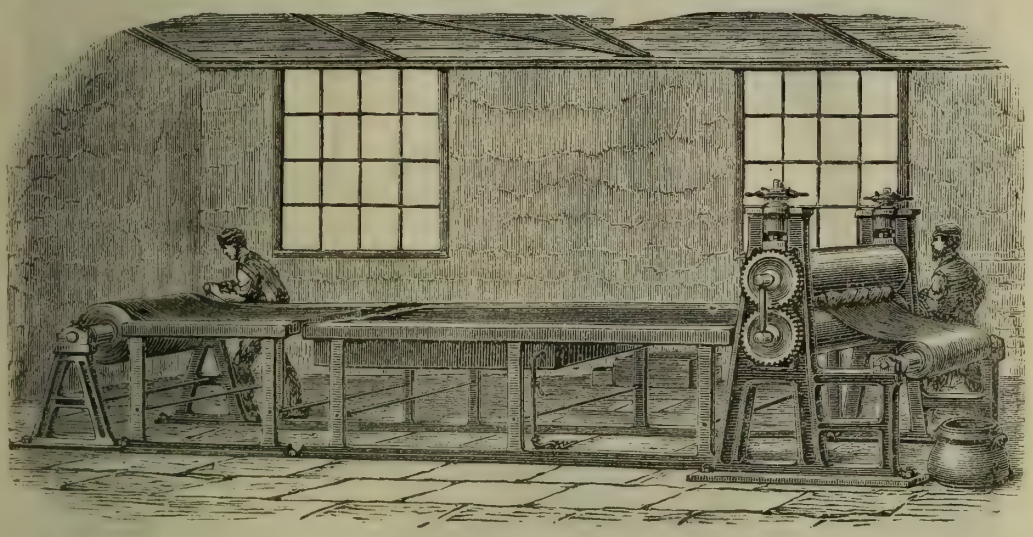
Manufacture of Waterproof Materials. — These generally consist of thin cloth, canvas, or some similar material, which is rendered impervious by being imbued with a solution of india-rubber. There are two distinct kinds of waterproof stuffs in commerce, the one being composed of a single layer of cloth, the surface of one side of which is covered with india-rubber, and the other description in which a layer of rubber is interposed between two layers of cloth. These are known technically as single and double fabrics. The double description is that more commonly called Mackintosh, from the name of its inventor, whose patent dates as early as June 17, 1823. The single fabric goods are of later date, and were introduced by Thomas Hancock, being patented the 17th October, 1837. The method of preparing the single fabric is as follows:—The india-rubber generally used is of an inferior description, and after having been subjected to a preliminary purification, is cut into pieces and placed in a suitable vessel, with about three, four, or five times its weight of a suitable solvent, the whole being then allowed to remain about three days. The solvent first employed was ether benzol, or the mixture of carbon disulphide and alcohol which has already been mentioned. At the present time coal-tar naphtha furnishes the most effective and economical solvent. The paste eventually produced, which may conveniently be of the consistence of very thick treacle, is placed on the stuff to be covered just at the moment that it is passing between two rollers. This operation is represented at Fig. 8. By the action of the rollers the liquid paste becomes spread equally over the surface of the cloth as a fine coating. After leaving the rollers the cloth passes over the surface of a sheet iron table heated by steam, and by this means the solvent used in preparing the pasty india-rubber is expelled, the cloth becoming by the time it reaches the extreme end of the table sufficiently dry to be wound off on to a suitable drum. The drying table has been considerably shortened in the drawing for the sake of convenience of representation; the ordinary length may be about 20 yards, but this necessarily varies with the

character of the solvent employed in the preparation of the rubber paste, and the rapidity with which the prepared cloth is being manufactured. In the preparation of Mackintosh the india-rubber paste is first spread on to one or both pieces of cloth, and the coated surfaces are then brought together and firmly attached to each other by passage through suitable rollers. In preparing this double stuff it is always a necessary precaution to have the under sheet of material a little wider than the upper, as by this means only can a perfect union of the edges be secured. Various attempts have been made from time to time to divest Mackintosh goods of the unpleasant smell with which they are always more or less associated; the best precaution, however, appears to consist in a thorough expulsion of the solvent used in the preparation.

Coating Telegraph Wires.—Wires are sometimes insulated by means of india-rubber in place of by gutta-percha. The method employed is generally that of doubling a band of rubber of suitable size round the wire, and uniting the freshly-cut edges by pressure. This is accomplished in the following way:—Long bands of rubber are first prepared by any of the usual methods, and slightly exceeding in breadth the exact size necessary; these then pass to a machine having two rapidly rotating circular steel knives, so arranged as to cut the edges of the india-rubber band obliquely. The band is then folded automatically over the wire to be coated, and the whole drawn through a perforated plate, whereby the freshly-cut edges of the rubber are pressed together, and so adhere, forming a perfect union.

India-Rubber Sponge.—This curious substance is produced by similar means to that patented by CHARLES HANCOCK in 1846 with reference to gutta-percha and its compounds. Ammonium carbonate or some readily volatilizable substance is mixed with

Fig. 8.

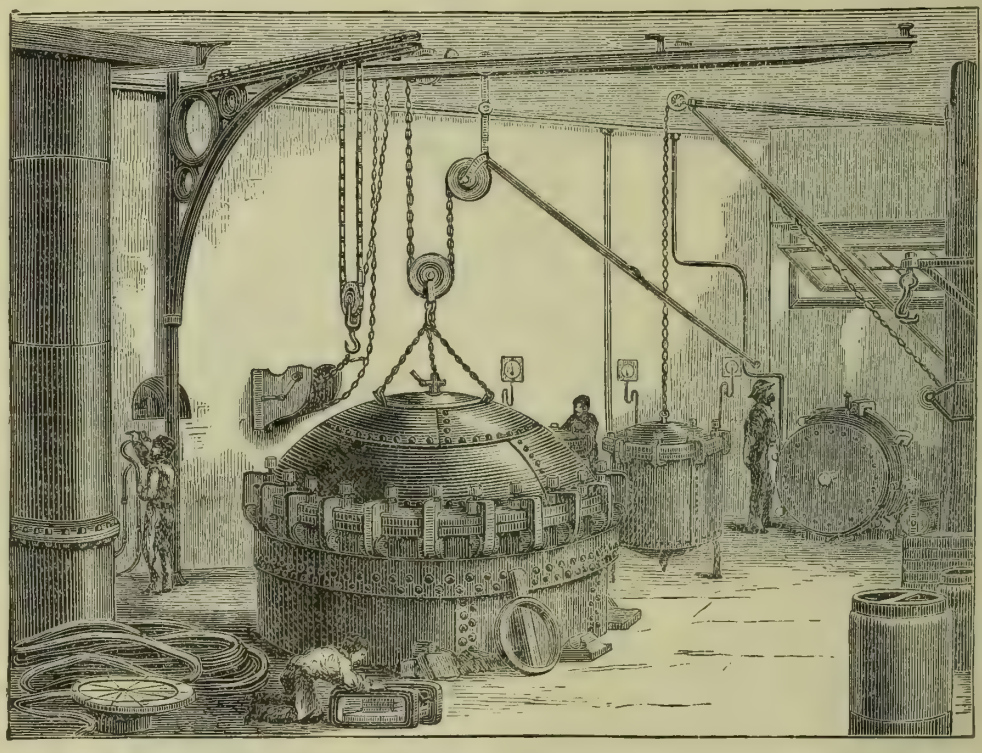


the rubber "in the masticator, or by other means." The mixture is subsequently heated, when it swells up and is converted into a spongy mass.

Vulcanization.—The discovery of the peculiar change which india-rubber experiences by the action of sulphur at a high temperature has been already noticed, as well as the names of the individuals to whom the world is indebted for the invention. HANCOCK'S original method of plunging the material into melted sulphur, as well as his modified process of vulcanizing by the vapour of sulphur or a volatile sulphide, are now seldom or never employed. The modern method is almost invariably that of mixing the india-rubber with the proper percentage of vulcanizing material, and subsequently exposing the mixture, after being moulded into the form which it is destined to permanently retain, to a temperature sufficiently high to effect what is termed "the change." This process is that universally adopted for all classes of articles, with the exception of those of a very thin description, or of those in which a surface vulcanization is sufficient, when a different mode is adopted, which will be subsequently described. Vulcanization is now technically called "curing," and the vessels in which the material is changed are called "curers." The first process to which the india-rubber is submitted, as a step to being vulcanized, is its intimate admixture with the necessary quantity of vulcanizing material, which is generally either free sulphur in the form known as "flowers of sulphur" (HANCOCK'S and GOODYEAR'S patents), or the orange sulphide of antimony (BURKE'S patent). Vulcanization by the latter substance is stated to afford a finished material of the highest degree of permanent elasticity and general durability. In either case the admixture of the vulcanizing agent with the india-rubber, which was formerly accomplished in the masticator, is now made by means of mixing rollers. The india-rubber in rough sheets is passed between a series of heavy rollers, under which is a shallow tray. The substance to be mixed with the rubber is strewn on to

the surface of the sheets, and by continued rolling and re-rolling the two materials become eventually thoroughly intermixed, and the combination is then ready for use. The rubber is then generally rolled into a sheet on to a layer of pounced cloth, the size of the usual sheets produced being 60 yards long by about 2½ to 3 yards wide, and weighing roughly about 200 lbs. Most of the articles made from vulcanized rubber are made from the sheet form of the material, which is pressed into moulds of the required form, the separate portions of which are screwed or otherwise securely clamped, and the whole is then placed in the "curer" and exposed to a suitable temperature for the necessary time. The moulds or the material must be "pounced"—dusted over with powdered steatite, chalk, or similar material, to prevent any adherence taking place in the subsequent heating. Tubing is prepared by wrapping bands of the prepared sheet india-rubber round iron mandrils of the required size, joining the edges with rubber cement, and finally wrapping the whole round with cloth or tape, and vulcanizing in the usual way. The curers employed for tubing and sheet india-rubber are frequently some 200 or 300 feet in length. Fig. 9 exhibits an ordinary circular curer employed for vulcanizing smaller articles; the lids of the vessels are, however, generally lifted by means of counterbalance weights in place of by chains wound by hand, as represented in the diagram. Sheet india-rubber is sometimes vulcanized by being simply pressed between two plates of iron heated to a suitable temperature, the sheet

Fig. 9



being allowed to remain for a sufficient time to effect the change.

With regard to percentages of material, temperatures, and duration of heating, each particular is modified by circumstances; the following details, however, will afford the reader some information on the subject:—

When sulphur is employed as a vulcanizing agent, with the object of producing an article possessing the maximum amount of durability and elasticity, the percentage employed is from about 7 to 10 per cent., the temperature about 260° Fahr. to 280° Fahr., and the duration of heating about three hours. With sulphide of antimony the degree of heat is about the same, the duration of heating being about two hours.

For the preparation of vulcanite, or ebonite, as it is more generally termed, the proportion of sulphur used is from 25 to 50 per cent., the degree of heat to about 400° Fahr., and the duration of heating from two to six hours.

In connection with the subject of vulcanization, it may be mentioned that the best effects are obtained from the admission of high-pressure steam directly into the vessels containing the articles to be cured. This appears to be the most favourable condition for the treatment of the articles, and, at the same time, no difficulty is experienced in keeping the heat uniform, or in regulating it to the required degree. It is almost superfluous to remark that the vessels have to be very strongly made, in order to bear the needful heavy pressure. The steam for ordinary articles

is generally of about 40 to 50 lbs. pressure per square inch, corresponding to a temperature of 260° to 280° Fahr. The less the percentage of vulcanizing ingredients used, the lower the temperature, and the shorter the duration of heating, the less the degree of vulcanization; whereas, on the other hand, increase in either agent employed, time of heating, or temperature, causes the "change" to become proportionally greater. The effect of over-curing is to darken the colour of the material, render it harder, and diminish its pliability; while, on the other hand, if the material be insufficiently vulcanized, all the advantages of the curing will not be secured. The point to be gained in the treatment is to secure all the desired advantages without overstepping the desired mark or failing from insufficient treatment, and this can only be obtained by an exact knowledge of the character of the materials employed, and experience in their use.

It now remains to describe the process employed for the surface vulcanization of comparatively thin articles, such as coated fabrics, &c. This is dependent on an important discovery made by PARKES, and patented by him, March 25, 1846. In this patent is claimed the use of a solution of chloride of sulphur in carbon disulphide as a means of vulcanizing india-rubber, either by admixture with the material, or by immersing the article for a short time in the solution. In practice the chloride of sulphur is dissolved in carbon disulphide, and the liquid thus produced sponged over the surface of rubber, as, for instance, a waterproof fabric. The article is subsequently placed in boiling water for about an hour. A curious feature in this method of treatment lies in the fact, that the vulcanization takes place at ordinary temperatures; but although this is the case, the process needs a certain amount of time for its effectual completion, and it is for the purpose of expediting the conversion that the heating by boiling water is adopted in practice.

An extensive use for a certain class of vulcanized rubber has developed of late years by its employment for palates and settings for artificial teeth. The so-called "dental rubber" of ASH & Co. commands an extensive sale for this purpose, the best qualities realizing as high a price as thirty shillings per lb. This rubber is made of various shades of pink, approximating to the natural colour of the gum. Other colours are also made from white to brown-orange, red, or black, the price varying from seven shillings to twenty-one shillings per lb. The preparation of these compounds is preserved a trade secret, the whole manufacture being conducted with the greatest exclusiveness. The dental rubbers are supplied in a form in which they become readily plastic at a moderate heat, so that the material can be moulded to the desired shape, and subsequently vulcanized, the vulcanizing material being already mixed with the rubbers before they are sent out from the factory. ASH & Co. supply dentists with portable vulcanizers, in which the curing process can be carried out. The temperature used varies from 270° to 320° Fahr., the time of heating being from fifty minutes to six hours (in extreme cases); the average duration of heating is, however, from fifty to one hundred and twenty minutes. The most curious feature of the dental rubbers is the fact of the light pink variety being capable of having its colour increased to any desired extent by immersion in ordinary spirits of wine and exposure to the sun, so that an exact imitation of the tint of the gum can be obtained. This process is technically termed "solarizing."

Compounds of India-rubber.—These are exceedingly numerous, some hundreds of patents having been taken out at different times for mixtures of india-rubber with various materials for a variety of purposes. All these mixtures (if we except vulcanizing compounds) tend to diminish the tensile strength of the material; but at the same time compounds are sometimes produced more applicable to special purposes than pure rubber. As an example of this, we need only specify kamptulicon and other similar materials so largely in use for floor covering. India-rubber is likewise for some purposes, such as making rough waterproof cloth, mixed with coal-tar, the mixture being spread on in the usual way. It is curious that mixtures of tar and india-rubber, when mingled with sulphur and heated, can be vulcanized without difficulty; the proportion of sulphur used is, however, somewhat greater than when pure rubber is employed. By a still further increase in the percentage of sulphur, afterwards heating the compound to 230° Fahr. for half an hour, and subsequently to from 300° to 320° for a further five hours, a hard compound resembling ebonite can be obtained.

Substitutes for India-rubber.—There have been several patents for materials to be used in place of india-rubber, the majority of them simply admixtures of rubber with various other substances. The only substitute in the real sense of the word, in any degree worth notice here, is that proposed in a patent of PARKES in 1855, whereby it was found that the addition of chloride of sulphur to drying oils, such as linseed and rape, had the effect of rendering them insoluble in their usual solvents, and it is at the same time remarked that oils so changed have the character of vulcanized rubber. There is, we believe, now made a material for waterproofing rough fabrics, the basis of which is made by exposing thin layers of a drying oil to a current of warm air for some time, when a substance is produced of an elastic nature, and capable of being vulcanized.

Recovery of Scraps of Vulcanized India-rubber.—This has often been attempted, but with only limited success. PARKES' method, patented in 1846, was to boil the fragments of material in a solution of chloride of calcium, whereby they become softened, and it is stated may be re-worked and again submitted to the vulcanizing process. In 1856 DODGE patented another method, founded on the alleged fact that a mixture of absolute alcohol and carbon disulphide would soften vulcanized rubber when digested with it for a short time. The pasty mass eventually obtained could then be used for any

desired purpose. In 1853 a patent was obtained by CRISTOPHER and GIDLEY for the utilization of scraps of vulcanized rubber. The process consisted in "macerating" the material in "a hot solution of carbonated alkali, or in a solution of hydrate of lime, or in hot water in which caustic lime is suspended." The object was the withdrawal of the sulphur. Another patent was granted to HANCOCK and PHILLIPS in 1847. This consisted in the reduction of the refuse vulcanized material into shreds and boiling them subsequently in oil of turpentine.

Patents respecting the Manufacture, Treatment, and Applications of India-rubber.—These are so numerous that it would be hopeless to endeavour to give even an abbreviated list having any pretensions to completeness within the limits of the present article, and we must therefore confine the description to those which are the most important or which possess some marked feature of interest in connection with the subject. Most of the more important patents have now expired; the list is arranged in order of date.

1791, May 2, SAMUEL PEAL.—First patent for application of dissolved india-rubber for waterproofing, the solution in spirits of turpentine to be spread over the fabric with a brush.

1823, June 17, C. MACKINTOSH.—Waterproofing fabrics by a solution of india-rubber in "coal oil."

1824, November 29, T. HANCOCK.—Application of india-rubber as a substitute for leather and "various other useful purposes."

1836, October 24, C. NICKELS.—Apparatus for treatment of crude india-rubber and for converting it into thread.

1837, April 18, T. HANCOCK.—Mastication of rubber described, and its conversion into sheets by passage between heated rollers. Waterproofing of cloth by means of rubber made into a paste by addition of coal oil or other solvent.

1843, June 27, A. PARKES.—Preparation of blocks of india-rubber from scraps of the material by softening with turpentine or naphtha, and subsequent union of the fragments into a mass.

1843, November 21, T. HANCOCK.—Reducing the clammy nature of rubber by mixing with it "silicate of magnesia," effected by mixing rollers. Treating india-rubber alone or combined with "asphalt" with melted sulphur, or mixing with sulphur, subsequently exposed to a heat of from 200° to 400° Fahr.

1844, January 30, 1846, W. E. NEWTON (a communication).—Vulcanization of india-rubber by a mixture of sulphur with the carbonate or oxides of lead.

1846, January 12, C. HANCOCK.—Treatment of gutta-percha; preparation of spongy masses from "gutta-percha and its compounds by admixture with carbonate of ammonia or other volatilizable substance and subsequent exposure to heat in ovens." (Several other claims which need not be here noted).

1846, March 18, T. HANCOCK.—Shaping articles of india-rubber, mixed with vulcanizing ingredients, on moulds, and subsequently vulcanizing, whereby the form of the articles was rendered permanent.

1846, March 25, A. PARKES.—Application of chloride of sulphur, dissolved in "bisulphide of carbon," coal naphtha, turpentine, &c., to the vulcanization of india-rubber, gutta-percha, or their compounds. Application of the liquid obtained by passing sulphurous acid over "granulated camphor" to the solution of india-rubber, &c.

1847, February 8, S. MOULTON.—"Treating india-rubber by combining therewith calcined and carbonate of magnesia, hyposulphite of lead, and the artificial sulphuret of lead, and subjecting it to a high degree of temperature."

1847, February 10, C. HANCOCK.—Manufacture and treatment of gutta-percha alone, or in combination with other substances.

1847, December 30, T. HANCOCK and R. PHILLIPS.—Recovery of scrap vulcanized material by treatment with oil of turpentine at a temperature of about 300° Fahr.

1849, January 11, C. NICKELS.—Improvements in masticating machinery.

1849, April 26, W. H. BURKE.—Application of precipitated sulphide of antimony as a vulcanizing agent.

1850, May 7, G. E. M. GERARD.—Use of alcohol to be mixed with ordinary solvents of india-rubber to facilitate solution.

1851, March 4, A. V. NEWTON (a communication from GOODYEAR)—Preparation of a hard substance suitable for a variety of purposes by treating india-rubber or gutta-percha with sulphur, and exposing them to a high temperature. (This patent is the first for the preparation of what is now called ebonite.)

1852, September 18, M. POOLE (a communication from GOODYEAR).—Producing hard compounds resembling horn or whalebone by subjecting to heat a mixture of coal-tar, india-rubber, and sulphur.

1852, September 30, M. POOLE (from GOODYEAR).—Application of substance described in patent, March 4, 1851, to manufacture of combs.

1852, November 7, M. POOLE (from GOODYEAR).—Manufacture of elastic sticks for umbrellas, &c., from same material.

1852, October 1, M. POOLE (communication from GOODYEAR).—Nine patents for other applications of the material described in patent of March 4, 1851.

1852, October 2, M. POOLE (from GOODYEAR).—Further applications.

1853, January 5, G. E. M. GERARD.—Treatment of india-rubber by manipulations conducted at a heat of from 220° to 240° Fahr., at which temperature the material "is susceptible of receiving and retaining a greater extension than in its natural state."

1853, April 7, C. NICKELS.—"Improvements in machinery for the mastication, &c., kneading or grinding india-rubber, gutta-percha, and other matters."

1853, June 16, W. CHRISTOPHER and G. GIDLEY.—Recovery of waste vulcanized scrap.

1853, July 15. C. GOODYEAR.—Three patents for application of substance described in patent of March 4, 1851, for new purposes.

1853, August 30, C. GOODYEAR.—Application of

same material to manufacture of "rules, graduated scales, and measuring instruments."

1855, October 22, A. PARKES.—Treating such oils as rape, linseed, &c., with chloride of sulphur to produce compounds resembling vulcanized rubber.

1856, January 18, M. S. DODGE (a communication).—Re-working of scraps of vulcanized rubber by treatment with alcohol and carbon disulphide.

1859, May 18, J. CHILDS.—Employing a hydrated substance, such as gypsum or lime, to generate steam and produce pressure in the vulcanizing process. (This method is now generally employed for small articles, such as artificial palates, which in being vulcanized are placed in moulds in ordinary plaster of Paris, and exposed to the requisite degree of heat in closed vessels called portable vulcanizers. The plaster gives sufficient steam to maintain the necessary pressure during the curing process.)

1859, August 9, F. L. LAWRENCE.—For a mixture of $3\frac{1}{2}$ lbs. india-rubber, $1\frac{1}{2}$ lb. sulphur. 1 lb. of vermilion, and $9\frac{1}{2}$ lbs. oxide of zinc (proportions may be varied); the compound constitutes a dental rubber, and it is stated in the patent that after vulcanization the substance will acquire a deeper red colour by exposure in a vessel of alcohol to the sun's rays.

1859, December 6, W. E. NEWTON (a communication).—Preparation of a white compound suitable for a variety of purposes, by the exposing gutta-percha or india-rubber to the action of chlorine gas.

1860, May 29, C. SCHIELE (a communication).—Improving the lubricant properties of oils by the addition of a solution of india-rubber in heavy paraffin oil.

1862, September 27, M. HENRY.—Application of light petroleum to the solution of india-rubber, gutta-percha, and their compounds.

1864, March 5, C. HUMFREY.—The use of light petroleum spirit as a solvent for chloride of sulphur in its application to the vulcanization of india-rubber.

1864, August 4, G. E. M. GERARD.—Cutting sheets or bands of vulcanized rubber into threads.

1865, January 20, B. F. STEVENS.—Preparation of a vulcanizable compound to be used for waterproofing and other purposes by the admixture of caoutchouc with boiled oil and sulphur.

1867, August 28, G. G. SANDY.—Rendering vulcanizable materials plastic by addition of petroleum spirit, so as to admit of being more readily moulded into any desired shape. The articles are baked previous to exposure to vulcanization in order to expel the solvent.

1867, September 28, M. HAMER.—Manufacture of india-rubber tubing by drawing strips of material through a trumpet-shaped orifice.

1868, March 19, W. HOOPER.—Exposing rubber after the ordinary cleansing process to a heat of 250° Fahr. in a closed chamber, by which treatment the material is rendered in a suitable condition for compressing into solid blocks without previous mastication.

1868, April 13, T. FORSTER.—Mixing disintegrated vegetable fibre with caoutchouc in order to produce comparatively light, tough compounds for a variety of purposes.

1868, April 21, G. COLES, J. A. JAQUES, and J. A. FANSHAWE.—Improved means of cutting india-rubber thread.

1871, April 15, A. G. DAY.—An improved elastic compound for use as a substitute for caoutchouc, and composed as follows:—Cotton-seed oil 14 lbs., linseed oil 14 lbs., asphaltum 8 lbs., coal tar 8 lbs., and sulphur 10 lbs. The whole exposed to a temperature of from 310° to 330° Fahr.

1873, February 17, T. CATTELL.—Purification of gutta-percha by solution and precipitation as in previous patent.

1875, October 15, G. MACLELLAN.—Utilizing the waste cuttings from the waterproof cloth manufacture for making a material stated to be heavier, more elastic, and less brittle than vulcanite.

The above list has been of necessity much abbreviated from lack of space; it, however, includes most of the patents of any value in connection with the manufacturing portion of the subject.

INK.—*Encre*, French; *Tinte*, German; *Atramentum*, Latin.—The liquid or viscous pigments used for writing and printing are all termed inks. The inks of antiquity were similar to the Indian or Chinese ink of the present day. PLINY and VITRUVIUS describe ink as a combination of soot or lamp black with glue or gum; DIOSCORIDES even mentions the proportions of three of the former to one of the latter. To these, according to some authors, the liquor extracted from the cuttle-fish was added.

PRINTING INK.—Printing inks are oils of various kinds more or less boiled or otherwise thickened, intimately mixed by grinding with finely divided lamp black or opaque colours.

The goodness or badness of printing ink depends mainly on the suitability of the menstruum with which the colouring body is mixed for the kind of work or machine on which it is to be used. Printing ink must distribute freely and work clean; it must not adhere to the type with too much tenacity; it must dry with great rapidity on the paper, and not at all on the type and rollers, and should never change colour. The varnish almost universally used up to the last ten years consisted of linseed oil boiled with great care till sufficiently thick, when it was on cooling intimately ground with lamp-black, driers of various kinds being added, according to the fancy of the ink-maker. The increased rapidity of printing has sent this old-fashioned ink almost entirely out of use, except for hand presses and the slower kinds of machines. For a detailed account of the mode of manufacturing printing inks, as at present practised, see PIGMENTS and VARNISH.

WRITING INK.—Writing inks are either coloured liquids, or liquids containing a finely divided precipitate suspended in it. The best black ink is a tannogallate of iron, and is made by adding an infusion of nut-galls to a solution of ferrous sulphate (copperas). The galls contain gallo-tannic and gallic acids; these on coming in contact with ferrous salts produce white precipitates, which turn black on

exposure to air; with ferric salts deep black precipitates are at once produced. A small quantity of gum is added to retain the precipitate in solution. Various colouring matters and dyes are sometimes added in order to reduce the cost of manufacture, but always with the effect of rendering the colour less dense or less permanent.

A good ink must be sufficiently liquid to flow freely from the pen; it must have a sufficiently strong colour to be distinctly legible when first written, and at the same time should not possess its full colour; it should to a very slight extent sink into the paper, where by subsequent oxidation its greatest depths of colour is developed. The ink is then very permanent, and cannot be easily effaced or erased. When ink consists chiefly of tannate of ferric oxide it is a dense black liquid, but rests merely on the surface of the paper, and it is therefore less permanent than when part of the black colour is in the paper itself.

The proportions used by different ink makers vary very much; Watts gives the following recipes:—

	Parts by Weight.					
Galls,	225	187	133	125	66	62
Copperas,	75	73	55	24	22	31
Gum Arabic,	25	73	55	24	19	31
Water,	1000	1000	1000	1000	1000	1000

The following is also a good recipe:—Boil 12 lbs. of Aleppo galls in 6 gallons of water for an hour, adding water to replace that evaporated; strain, and again boil the galls in 4 gallons more water for half-an-hour; strain, and boil again with 2½ gallons more water; strain, and mix the liquors. Add 4½ lbs. of coarsely powdered green copperas, 4 lbs. of gum Arabic in small pieces; agitate until the ingredients are dissolved, and filter through a hair sieve. This will yield about 12 gallons of very fine durable ink.

The bruised nut-galls are boiled for three hours with three-fourths of the quantity of soft water to be used in the finished ink; fresh water being from time to time added to replace loss by evaporation. The decoction is then drawn off into a tall vessel and allowed to settle, the clear liquor being drawn off, and if necessary strained through a hair sieve.

The gum is dissolved in a small quantity of hot water, the solution filtered, and then added to the clear decoction of galls.

The ferrous sulphate is in like manner separately dissolved in as small a quantity of water as possible, and then well mixed with the decoction containing the gum. Water is then added to bring the amount up to the desired total, and the whole exposed to the air with occasional stirring until the colour has attained the required depth. When a moderately deep tint has been obtained, the ink should be drawn off clear into bottles and well corked up. Some makers digest rather than boil the galls.

The decoction of galls is by some makers exposed to the air for some days with frequent agitation before the copperas is added, with the view of increasing the amount of gallic acid by oxidation of the tannin. In this case a larger amount of logwood may be used.

Logwood, besides being a strong colouring matter, contains also tannin, and is therefore profitably used in making the cheaper kinds of ink.

Sumach and oak bark, and the wood and bark of most trees containing tannin, have been from time to time used in the manufacture of low priced inks. In any case not more than half the amount of copperas will be assimilated that can be taken up when gall nuts are used.

The following recipes for logwood inks have been collected by Watts:—

	Parts by Weight.				
Galls,	50	174	50	60	42
Logwood,	—	—	100	20	21
Copperas,	32	87	16	20	21
Sulphate of copper,	—	—	—	—	5
Gum,	9	43	47	20	16
Sugar,	—	—	23	1000	—
Vinegar,	125	135	—	—	—
Water,	1000	1000	1000	1000	1000

Sulphate of copper deepens the colour of the precipitate, but renders it more likely to settle down. Sugar renders the ink more fluid, and permits the addition of a larger proportion of gum. It likewise renders the ink adhesive when dry, so that a copy of the writing may be taken off by laying a damp sheet of unsized paper upon it, and passing lightly over it a flat iron moderately heated, or by applying a little pressure in the cold. Ink of this quality is called *copying ink*.

Ink, as it is usually prepared, is very apt to undergo certain changes, which render it unfit for use; of these, three are the most important:—1, its tendency to become mouldy; 2, the liability of the black colouring matter to separate from the fluid, the ink then becoming what is termed ropy: 3, its loss of colour, the black changing to brown, and at length almost entirely disappearing.

Mouldiness is prevented by adding a few drops of carbolic acid, creosote, some essential oil, or finely-bruised cloves, first mixed with strong acetic acid.

The separation of the colouring matter is retarded by adding a small quantity of an acid, the ferrous salt being thus hindered from passing into the ferric salt.

The change of colour can only be prevented by taking care that the copperas is not in excess of the gallo-tannic acid, by keeping the ink excluded from the air, and by avoiding the use of any mineral acid. If the ferrous sulphate is in excess, although the ink may be at first very black, it will subsequently become brown, and then yellow. The discoloration of ink in old documents is frequently due to the chlorine compound used in bleaching the paper not having been entirely removed. With the present modes of making paper this accident is not likely to occur.

The addition of acids to ink retards the oxidation of the ferrous precipitate, so that the ink only attains its full depth of colour after exposure to air. But in this case the addition of a small quantity of sulphindigotic acid or sulphindigotate of sodium (indigo carmine) is necessary to give colour to the ink on first using it. Stephens' writing fluid is thus made.

To prepare this ink, exhaust 40 parts by weight of nut-galls with 112 parts of water; to the filtrate add 7 parts of ferrous sulphate, and a quarter of a part oxalic acid. The sodium sulphindigotate is made by dissolving 1 part of finely-powdered indigo blue in 4 parts weight of fuming sulphuric acid, allowing the mixture to stand for twenty-four hours, and then diluting it with water, and adding carbonate of sodium till the acid is almost saturated. The precipitate is well washed, mixed with a small quantity of water, and then added to the ink till the latter assumes a deep greenish-blue colour.

Or, take 15 parts of bruised gall-nuts, boil for about an hour in 200 parts of water, strain, and then add to the liquor 5 parts ferrous sulphate, 4 parts fine iron turnings or filings, and a solution of half a pint of powdered indigo in 3 parts of sulphuric acid. This ink writes green, but turns black after a few hours. It flows very freely from the pen.

Another recipe for making the ink on a small scale directs:—Blue Aleppo galls, 4½ ozs.; bruised cloves, 1 dram; cold water, 40 ozs.; ferrous sulphate, 1½ oz.; sulphuric acid, 35 minims; neutral sulphate of indigo, ¼ oz. Place the galls, when bruised with the cloves, in a 50 ozs. bottle, pour the water upon them, and digest, shaking daily for a fortnight. Then filter through paper into another 50 ozs. bottle, next put in the iron, dissolve completely, and filter; add the acid and mix thoroughly by shaking; lastly add the sulphindigotic acid, and after shaking well pass the whole through paper filters out of one bottle into the other till the operation has been completed.

Chrome Ink.—Runge, after endeavouring for a long time to find a black fluid possessing the properties of forming no deposit, of adhering strongly to the paper, of being unaffected by acids, and lastly, of neither acting nor being acted upon by steel pens, succeeded after many experiments. His composition has the advantages of being very simple and exceedingly cheap. It is prepared by adding 1 part of chromate of potassium to 1000 parts of a saturated solution of logwood, made by boiling 22 lbs. of logwood in a sufficient quantity of water to give 14 gallons of decoction; to this liquor, when cold, the chromate is gradually added, and the mixture well stirred. The addition of gum is injurious. In the preparation of this ink, it must be remembered that the chromate, not the bichromate, of potassium is employed, and that great care is requisite to insure the due adjustment of the relative proportions of the ingredients used. The best way is to make the decoction of logwood, and *gradually* add to it, well stirring the mixture, as much solution of chromate as will give the desired shade.

It appears astonishing, says Runge, what a small quantity of chromate of potassium is required to convert a large amount of decoction of logwood into a black writing fluid; care must be taken not to allow the proportion of chrome salt to exceed 1 part for 1000 parts of decoction of logwood, as a larger quantity exercises a prejudicial effect in destroying the tinctorial matter of the liquid, whilst, in the proportion above mentioned, a deep blue-black writing ink is formed, which, unlike the ink made with tanno-gallate of iron, is perfectly fluid, forming no deposit. This fluid possesses another advantage; the paper which has been written upon with it may be washed with a sponge, or be left twenty-four hours under water, without the marks being erased. Gobel takes 24 parts of solid commercial extract of logwood, 1000 parts of water, and 2 parts of yellow chromate of potash.

Indelible Ink.—Various compositions have been devised; they all depend on the suspension of finely divided carbon (Indian ink, Chinese ink, or lamp black) in either common ink or some dark-coloured fluid. Traill's ink is prepared by steeping gluten, obtained in the ordinary way, in water for twenty-four to thirty-six hours, and then digesting it in strong acetic acid, 3 parts of gluten to 20 of acid, specific gravity 1·033. By the aid of a gentle heat a greyish white fluid is obtained, which can hold the black colouring matter in suspension, from 8 to 12 grains of fine lamp black and 12 grains of indigo are ground in with each fluid ounce of the fluid.

The vehicle of Stephen's indelible ink consists of shellac or resin dissolved in an alkaline solution of potassium or sodium carbonate. About equal weights of the alkali and the resin are intimately mixed, the requisite quantity of water added to bring the ink to the proper consistence, and the whole boiled till the greater portion of the resinous substance has dissolved. The carbon is then added. A black liquid will thus be produced, which when mixed with any suitable coloured solution forms an indelible ink.

Vanadium Indelible Ink.—Berzelius made a beautiful fluid ink, containing no precipitate, but of an intense black colour, by mixing a decoction of galls with vanadate of ammonium. This ink is not destroyed by chlorine, though its colour is altered; it is unaffected by alkalies; acids turn it blue.

A splendid ink has been made by Robert Pinkney, of the firm of Blackwood & Co., who discovered that vanadium can be most advantageously substituted for copper in the formation of aniline black; and he employed this reaction for the preparation of a permanent ink. A few grains of vanadium, say from 7 to 12, are sufficient to produce, together with hydrochlorate of aniline and chlorate of sodium, a gallon of indelible ink.

Copying Ink.—The addition of sugar to ink in the proportion of 6 ozs. to the gallon, or of a small quantity of glycerin, causes the ink to retain so much moisture that it never becomes really dry on the paper. On bringing more moisture in contact with this damp ink it becomes again fluid. On pressing strongly against it, therefore, a moist sheet of thin unsized paper, the ink is liquefied, and is absorbed in the pores of the paper immediately above it: the writing is read through the paper.

Runge's ink forms a very good copying ink.

Violet-black Rouen ink is prepared by boiling 750 parts of logwood with 6000 parts of water, 35 parts of alum, 31 parts of gum Arabic, and 15 parts

of sugar candy, leaving the mixture to stand for two or three days, and straining through a linen cloth.

Another violet-black copying ink is made by mixing 60 parts of vinegar with 70 of water, and dissolving these in 4 parts by weight of commercial logwood extract, 3 parts of copperas, 2 parts of alum, 3 parts gum Arabic, and 5 parts of sugar.

Ink Powder.—Aleppo galls, 3 lbs.; copperas, 1 lb.; gum Arabic, ½ lb.; white sugar, ¼ lb. All the ingredients to be finely pulverized and mixed; 2 ozs. dissolved in 1 pint of boiling water gives a very good ink.

Or, mix intimately 4 parts of powdered gall nuts with 2 parts of green copperas and 1 part of gum Arabic.

Solid Chrome Ink.—1 part potassium chromate, 100 parts solid extract of logwood, one-tenth of indigo carmine, the whole to be thoroughly ground.

Coloured Writing Inks.—Most of the coloured vegetable extracts and the aniline colours used in dyeing serve well as coloured inks. Aniline violet has especially come largely into use as an ink.

Red Ink.—The most permanent colour is a decoction of Brazil wood, to which stannous chloride or cream of tartar and alum has been added, and thickened with gum water. For example, 2 lbs. of ground Brazil wood are added to 3 gallons of vinegar, and the liquor boiled till reduced to 1½ gallon: 1½ lb. of rock alum is then added. Or: 4 parts of Brazil wood in 60 parts water; boil down to 36 parts; filter, and mix with one-eighth of stannous chloride (tin salt) and one-fourth part of gum Arabic. Again: 8 parts of Brazil wood are boiled in 120 parts of water, with 2 parts of alum and 2 parts of cream of tartar; the liquid is concentrated to half its bulk, and 2 parts of gum Arabic and 2 parts of sugar are finally added.

Cochineal inks are far more brilliant, but their colour is less lasting. The best is a solution of carmine in caustic ammonia; it must be kept in well-stoppered bottles. One part of carmine, 120 parts ammonia, with 1½ part of gum Arabic, are, according to Böttger, good proportions.

Or, mash 12 parts of powdered cochineal with 4 parts of carbonate of ammonium in 32 parts of hot water; digest, and pour off the clear liquid.

Addition of a mixture of cream of tartar and stannous chloride produces a more scarlet tint, while cream of tartar and alum render the ink more crimson.

Stephens' Red Ink.—Add to a quantity of common carbonate of potassium, sodium, or ammonium, twice its weight of crude argol in powder. When the effervescence has ceased, decant or filter the solution from the insoluble matter, and add by measure half its quantity of oxalate of aluminium, prepared by dissolving damp, newly-precipitated alumina in as small a quantity as possible of a concentrated solution of oxalic acid. The mixture thus prepared is next coloured, when cold, with bruised or powdered cochineal, and after standing for forty-eight hours is strained, when it is fit for use.

Blue Ink.—There appears to have been no permanent blue ink until Stephens found the means of dissolving Prussian blue so as to adapt it to the purpose. The ink is prepared as follows:—Take Prussian blue, put it into an earthen vessel, and pour upon it as much strong acid as will cover it. Hydrochloric, nitric, and sulphuric acids are equally of service; but if the latter be used, it should be diluted with a quantity of water equal to its own bulk. The Prussian blue is allowed to remain in the acid from twenty-four to forty-eight hours, or even for a more extended period; the mixture is then diluted with much water, at the same time agitating it, for the purpose of washing from it the salts of iron. When in this state of dilution it is permitted to rest until all the colour has subsided, at which time the supernatant liquid is siphoned off, and a further quantity of water added. This process is repeated until ferrocyanide of potassium no longer gives a blue precipitate; and also until the liquid ceases to redden blue litmus paper, thus proving that the acid has been entirely removed. The product is then placed upon a filter, and suffered to remain until all the liquid has drained away. The Prussian blue by this treatment has lost a considerable proportion of its iron, and is now more readily acted upon and dissolved than in any other condition. After being gently dried, oxalic acid is added to and carefully mixed with the Prussian blue; cold distilled water is then poured, in small portions at a time, over the whole, making it into a dense or dilute solution, according to the depth of colour required. The amount of oxalic acid may be varied according to the quantity of water used. Prussian blue, in its ordinary state, will require two or three times its weight of oxalic acid, and even then it will be liable to precipitation after standing; when deprived of a portion of its iron in the first place, by means of acid, it remains a permanent solution.

Ohme recommends the following formula for blue ink:—Dissolve 1 scruple of iron in nitro-hydrochloric acid (aqua regia), filter the solution, and dilute it with sufficient water to make 8 ozs., which is mixed with 4 drachms of ferrocyanide of potassium, previously dissolved in 8 ozs. of water. The resulting subsidence is collected on a filter, and after the fluid has as far as possible been removed, the precipitate is washed with pure water, until the latter passes through having an azure tint. As soon as this occurs, the funnel and its contents are placed over a clean vessel, the filter pierced, and the blue compound washed with 24 ozs. by weight of water. This latter constitutes the blue ink, the formation of which depends on the property of the precipitate to dissolve in pure water, and not in solutions of other salts.

Purple Ink.—To produce a purple-coloured ink, called the *king of purples*, Normandy recommends the following method:—To 12 lbs. of Campeachy logwood add as many gallons of boiling water; pour the infusion through a funnel with a strainer made of coarse flannel on 1 lb. of hydrate or acetate of copper (verdigris), finely powdered; at the bottom of the funnel a sponge is placed; then add immedi-

ately 14 lbs. of alum, and for each 17 gallons of liquid add 4 lbs. of gum Arabic or Senegal; let these remain for three or four days, and a beautiful purple will be produced.

Green Ink.—Klaproth directs for the preparation of green ink that 2 parts of acetate of copper and 1 part of bitartrate of potassium be boiled in 8 parts of water, till the solution be reduced to half the bulk. It is then filtered through cloth, and, after cooling, bottled.

Winckler has given the following recipe for a green ink:—Dissolve 180 grains of bichromate of potassium in 1 fluid oz. of water; add to the menstruum, while warm, half an ounce of spirit of wine; then decompose the mixture with concentrated sulphuric acid until it assumes a brown colour. The liquor is now evaporated till it is reduced in quantity to one-half, when it is diluted with 2 ozs. of distilled water, filtered, mixed with half an ounce of alcohol, subsequently with a few drops of strong sulphuric acid, and then allowed to rest till after some time it assumes a beautiful green colour. A small quantity of gum Arabic is finally added.

Yellow Ink.—Yellow ink, according to Ure, is prepared by dissolving 3 parts of alum in 100 parts of water, adding 25 parts of bruised Persian or Avignon berries, boiling the mixture for an hour, filtering the liquor, and dissolving in it 4 parts of gum Arabic.

Gold and Silver Inks.—Gold ink is prepared as follows:—Grind upon a porphyry slab with a muller gold leaf and fine white honey, or glycerin, till the gold is reduced to an impalpable powder. The paste is then carefully collected and diffused through water, which dissolves the honey, or glycerin, causing the deposition of the precious metal; the water must now be decanted, and the sediment washed to free it from the saccharine matter. The powder when dry is very brilliant, and when required for use is suspended in mucilage of gum Arabic. After the writing executed with this ink is dry, it should be burnished with ivory.

Silver ink is prepared in the same manner, by substituting this metal, in leaf, for the gold.

Indian or Chinese Ink consists essentially of lamp black formed into cakes by means of some glutinous or adhesive substance, such as gum water. The lamp black is said to be made in China by collecting the smoke of the oil of sesamé; and M. Merimée states that the Chinese do not use glue in the fabrication of their ink, but certain vegetable juices, which render it more brilliant and more indelible upon paper. Proust says that lamp black, purified by potash lie, when mixed with a solution of refined glue, and dried, formed an ink which was preferred by artists to that of China. A good Indian ink may be made with ivory black, ground to a fine powder, made into a paste with weak gum Arabic water, and then formed into cakes.

Marking Ink.—These inks are solutions containing silver, which by means of heat or light, or both, is reduced in the tissues, producing an intense black stain, which with ordinary usage is very permanent.

Subjoined is a very common formula for this kind of ink:—

Six drachms of nitrate of silver are dissolved in 3 ozs. of distilled water, and as much ammonia is added as will liquefy the precipitate which it at first occasions. A little sap-green, ivory black, Indian ink, or indigo, diffused through 4 drachms of mucilage of gum Arabic, forms the temporary tinctorial matter, and water is added to make up the quantity to 4 ozs.

Many marking inks, although black when first applied to the linen, become gradually washed out, and a yellowish stain only remains. Jules Guiller has given three recipes for marking ink, which he believes to be free from these and some other prevalent evils. They are as under:—

For the first ink, 22 parts of carbonate of soda are dissolved in 85 of distilled water, and 20 parts of pulverized gum Arabic are diffused through the menstruum: 11 parts of nitrate of silver are then liquefied in 20 parts of ammonia, and this is commingled with the alkaline solution. The mixed fluids are next warmed in a flask, by which they become greyish-black and partly coagulated, subsequently brown and clear; then, when ebullition commences, very dark, and of such a consistence that it will flow readily from the pen. This ink and that prepared from the next formula have the advantages that no precipitates are formed in them. For the second ink take,—

	Parts.
Nitrate of silver,	5
Distilled water,	12
Powdered gum Arabic,	5
Carbonate of soda,	7
Ammonia,	10

Treat these ingredients in the manner last described, and heat the resulting mixture in a flask until it has acquired a very dark tint, which is generally the case when its volume has diminished by evaporation about five per cent. By continuing the evaporation too long, a precipitate is occasioned in consequence of the loss of volatile alkali. The ink prepared in this manner is distinguished by producing very black characters upon linen, and is very suitable for marking with stamps or stencil-plates.

According to the third prescription, 22 parts of carbonate of soda are dissolved in 25 of distilled water, as also 17 parts of nitrate of silver in 42 parts of ammonia; 20 parts of gum are then liquefied in 60 parts of water, and mixed with the soda solution, and afterwards with that of nitrate of silver, and lastly, 33 parts of sulphate of copper are added. This writes a rich blue.

Redwood's ink is prepared in the following manner:—

Dissolve 1 ounce of nitrate of silver, and $1\frac{1}{2}$ of crystallized carbonate of soda in separate portions of distilled water, and mix the solutions; collect the resulting precipitate on a filter, wash it well with distilled water, and introduce it while still moist into a Wedgwood-ware mortar; add 8 scruples of tartaric acid, and triturate the whole until effervescence has ceased; next add a sufficient quantity

of ammonia to dissolve the tartrate of silver; mix in 4 fluid drachms of archil, 4 drachms of white sugar, and 12 of finely powdered gum Arabic; and pour in as much distilled water as will make 6 ozs. of mixture.

The essential distinction between this and ordinary inks is the use of tartrate instead of nitrate of silver.

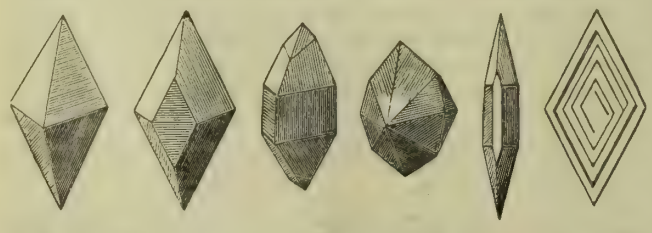
Reade's ink, which may be used with steel pens, and the colour of which is readily developed by application of heat, is prepared as follows:— Nitrate of silver is triturated in a mortar with an equivalent of desiccated tartaric acid. Water is then added, which causes the separation of crystals of tartrate of silver, nitric acid being set free. The latter is neutralized carefully by adding ammonia, which also dissolves the metallic tartrate. Gum, colouring matter, and water are subsequently added in quantities which may be varied at pleasure.

IODINE.—*Iode*, French; *Iod*, German; *Iodum*, Latin. Symbol, I. Atomic weight, 127.—This element was discovered by Courtois in 1812. Courtois was a manufacturer of saltpetre in Paris, and in treating the potash salts from kelp or varec with calcium nitrate suffered considerable loss from the rapid corrosion of his copper pans used for evaporation. After the most patient researches he succeeded in isolating this important element. The discovery was announced through Clement-Désormes to the French Institute, at a meeting on the 29th of November, 1813. It created great interest, and was immediately investigated by Gay-Lussac and Davy, and later by Ure, who made it in some quantity. The discoverer was unsuccessful as a manufacturer; he died in poverty, and his widow was a pensioner of the Pharmaceutical Society of Paris.

The name is derived from the Greek word for violet (*ἰον*), in allusion to the colour of its vapour.

Properties.—Iodine at ordinary temperatures is a crystalline solid, and presents a greyish-black appearance and a metallic lustre very similar to that of black-lead or specular iron ore. The crystals are modifications of an elongated octahedron with a rhomboidal base, the primary form belonging to the

Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5. Fig. 6.



right prismatic system. See Figs. 1, 2, 3, 4, 5, and 6. The finest crystals are obtained from its solution in ether. By sublimation it is obtained in laminæ, or broad oblique tables, which, when thin, transmit light of a red colour, according to Gmelin; but Payen states that the crystals which form under the microscope, and do not exceed in thickness the $\frac{2}{1000}$th of a millimétre, or ·000787 of an inch, are not translucent. Iodine is soft and friable. Sp. grav. 4·948. It is a non-conductor of electricity. Iodine fuses at 224·6° Fahr. (107° C.), and boils between 347° and 356° Fahr. (175° to 180° C.), giving a splendid violet vapour, which condenses in crystals upon a cold surface. At ordinary temperatures it is subject to spontaneous evaporation, especially if moist, giving off an odour resembling chlorine. When in a thin stratum the vapour of iodine presents a beautiful rich violet shade; but if examined in a layer 4 inches thick it presents the appearance of a black mass, impervious to light.

Vapour of iodine is the heaviest of all known gases, being, according to the investigations of Dumas, of spec. grav. 8·717, and by calculation from its atomic weight, 8·801. Alcohol and ether dissolve it readily, producing dark reddish-brown liquids. It is soluble in 10 to 12 parts of alcohol; the solution gradually undergoes decomposition; on the addition of water iodine is precipitated as a brown powder. Water dissolves only $\frac{1}{7000}$th of its weight. The solvent action is increased, however, when there are other salts, such as nitrates or chlorides, present. In either case a brownish liquid is formed, which by long exposure disappears, the iodine being transformed into iodic and hydriodic acids. It is very soluble in chloroform, bromoform, bisulphide of carbon, benzine, and petroleum, giving deep red to violet solutions; also in methylic and amylic alcohols, aldehyde, glycerin, and creosote. Many of the essential oils dissolve it; but some are decomposed by it, *e.g.*, oil of turpentine, in which the solution is followed by explosion. It is readily soluble in hydriodic acid and in aqueous solutions of some metallic iodides. A solution of 1 part of potassium iodide in 2 parts of water will dissolve 2 parts of iodine.

These solutions have two well-marked distinctions in colour, one series being red by transmitted light, like solid iodine, the other violet, like its vapour. Alcohol, ether, ethyl bromide, Dutch liquid, benzol, glycerin, and potassium iodide represent the former series of solvents. Bisulphide, tetrachloride, and monochloride of carbon, chloroform, phosphorus terchloride, tin tetrachloride, and chloral, represent the latter series.

In its reactions iodine resembles chlorine and bromine, but is less energetic, and is displaced from most of its combinations by these bodies. It unites with most of the non-metallic elements, producing with some (such as nitrogen) highly explosive compounds; and with others (oxygen and hydrogen, for example) acids which are capable of forming salts, many of which are very important. Iodine has a strong affinity for, and forms iodides with most of the metals. Iron and zinc are speedily attacked, and in the presence of water dissolved, forming iodides. The mineral acids displace iodine from the iodides, and set it free. A characteristic and remarkable

property of iodine, discovered by MM. Colin and Gaultier de Claubry, is the blue coloration it affords when brought in contact with starch-paste disseminated in water. This is so delicate and characteristic, that it still remains *the* test for iodine in all investigations, affording as it does a perceptibly blue tinge when not more than $\frac{1}{1000000}$th part of iodine is contained in the liquid.

Iodine has a strong affinity for hydrogen, and acts as a mild bleaching agent and a good deodorizer. It is a most valuable therapeutic agent, and as such was first brought into notice by Coindet, a distinguished physician of Geneva, who found it an effectual remedy for goitre. Administered as iodide of potassium, its application is frequent, more especially in diseases of the skin, and as an absorbent for eradicating glandular enlargements, indurations, thickening of membranes and tumours, as well as in several other ailments. When applied to the skin the cuticle becomes coloured of an orange yellow, but this disappears after a short time. Iodine in considerable doses acts as an irritant poison. In such cases the stomach pump and copious libations of amylaceous liquids should be resorted to. In continued small doses it accumulates in the system, and produces the severe general symptoms known as "Iodism;" hence the necessity of keeping bromide of potassium, now taken in large and repeated doses, free from all traces of iodide.

Sources.—Numerous researches have shown that iodine is one of the most widely disseminated elements, although it may be remarked that the aggregate amount procurable is comparatively small. It is not found in the free state, but in combination is distributed over the animal, vegetable, and mineral kingdoms. In the mineral kingdom it is met with, combined with silver, mercury, and lead, in ores from Mexico and Chili, and also in Spain; in Silesian cadmiferous ore it is found combined with zinc; and it has been detected in a species of lead ore from South America; it is contained as potassium iodate in the caliche of Chili, and has been detected as iodide of sodium in the rock-salt of Hall and in the Tyrol. It has also been found in the dolomite of Saxony, in the limestone of Lyons and Montpellier, and the shale of Sweden; also in the coal of Silesia and the peat of Klobach. Many springs have been found to yield quantities of iodine combined with potassium, sodium, magnesium, and calcium; of this description are the waters of Bex, Sülze in Mecklenburg, Kolberg in Pomerania, Salzuffeln and Konigsbronn, near Unna, Rehme, near Minden Schönebeck, Halle in Saxony, Dürrenberg and Kösen, Artern and Salzungen, Schonalkalden, Salzhausen and Kreuznach, Bolechow and Drochobycz in Galicia, Kenahwa in North America, Guaca in the province of Antiogena in New Granada, and Jalliez in France. Its presence has likewise been proved in the following mineral waters: in the thermal spring of Albano, in one near Sales in Piedmont, in several salt springs near Ascoli, in the hepatic waters of Castel Nuovo d'Asti, in the hot spring of Aix in Savoy, in the Bonnington water near Leith, in Bath water, in the water from Marienbad in Bohemia, and also in the waters from Carlsbad, Heilbrunn, and Kunzig in Bavaria; in the medicinal waters of Hall in Austria, used for the cure of goitre; in the hepatic water of Trutkawiec, and in the alkaline waters of Iwonicz in Galicia. Besides these, later investigations have proved its presence in several other mineral waters. The best known of these are the following:—Castellamare, Challes, Cheltenham, Colberg, Friedrichshall, Hassfurt, Heilbrün, Homburg, Carlsbad, Leamington, Pyrénées, Sales, Salzchlurt, Seidschutz, Urma, and Vichy. Some of the springs of Tuscany contain considerable quantities of iodine. The Genoch Watoe spring of Java contains ·0138 per cent. of iodide of sodium. The phosphate of lime from Lot and Tarn-et-Garonne contains considerable amounts of iodine, and methods have been proposed for extracting it from this source. The most important mineral source is the caliche of Peru. This is now worked so largely for the manufacture of nitrate of soda, that although the proportion of iodine is small, it bids fair to become the largest source of this element. The mother liquids from the nitrate of soda contain, according to Reichardt—

Chloride of magnesium,	1·121
Chloride of sodium,	8·594
Sulphate of magnesium,	2·214
Nitrate of sodium,	23·300
Iodate of sodium,	·440
Water and loss,	64 331
	100·000

A specimen tested by Tatlock gave iodine = 1·14 per cent. of iodide of sodium. The iodine in the caliche has been estimated at ·16 per cent., or 3·58 lbs. to the ton. In 1875 about 300,000 tons of nitrate of soda were exported. This is equal to about 600,000 tons of caliche; if therefore this estimate be correct, the amount of iodine thus available would be 18,750 cwts., or more than five times the total present production from other sources; probably, however, ·1 per cent. may be nearer the average proportion, and if only one-half of this could be extracted it still represents 6000 cwts. The extraction of iodine from this source, however, presents many practical difficulties, and but a comparatively small portion has yet been exported. The actual quantities exported were in 1874, 497 cwts., 1876, 900 cwts.—the latter the outcome of five factories working, of which the estimated produce was expected to be about double this quantity.

In the vegetable kingdom all the *Algæ*, and also the marine plant *Zostera marina*, contain iodine. It has also been found in certain land plants—in tobacco, in a species of *Salsola* growing in floating gardens in the fresh water lakes of Mexico, in *Lichen confinis*, *Statice armeria*, and *Grimmia maritima*, growing upon rocks on which sea-water has been blown by the wind. The ashes of several shore-plants, such as the different kinds of *Salsola*, and such as are used for producing the *barilla* of Spain and the Sicilian soda, contain little or no iodine. A vast amount of iodine exists in the ocean. Balard has found it in the Mediterranean, and Plaff in the

Baltic, but from the minute proportion in which it is present, Davy, Gaultier, Fyfe, and others, failed to detect it. It cannot be detected in sea-water by the ordinary methods of analysis; according to Sonstadt, it exists in sea-water in the form of calcium iodate, and by reducing this with sulphurous acid, and then estimating the iodine, he has calculated that 250,000 parts of sea-water contain 1 part of calcium iodate, and that a cubic mile of sea-water contains 11,072 tons of iodine. However difficult of detection in sea-water, it is found in considerable quantity in certain of the *Algæ*, which have the power of eliminating this element from sea-water and concentrating it in their tissues. It is a remarkable fact, that although bromine exists in much larger quantity in sea-water, and can be readily detected and extracted from it, these *Algæ*, though they all contain bromine, do not take up more than a tenth the amount of this element as compared with iodine. The relative proportions in sea-water are, according to Sonstadt:—

Bromine,	1 part in	3333	parts.
Iodine,	1 " "	368,110	"

Others put the proportion of iodine as 1 in 30,000,000, the truth, probably, lies between the two estimates. Stanford has shown by a large number of analyses that although the *Algæ* contain iodine, only a few of the common species contain it in quantity.

The following table shows the proportion of iodine contained in 100 parts of the dried *Algæ* according to various authorities:—

	Sarphati.	Schweitzer.	Godechens.	Zenger.	Wallace.	Stanford.
Laminaria digitata	·135	—	·625	—	·4440	Stem, ·4535 A; Frond, ·2946 B
Laminaria saccharina	·230	3·88	—	—	·2280	·2794 C
Fucus serratus	·124	·058	·177	—	·0565	·0856 D
Fucus nodosus	—	—	·074	—	·0396	·0572 E
Fucus vesiculosus	·001	—	—	—	—	·0297 F
Zostera marina	·0005	—	—	—	—	·0457
Rhodomela pinnastroides	—	—	—	—	—	·0378
Hydesia siliquosa	—	—	—	—	—	·2131
Hymanthalia lorea	—	—	—	—	—	·0892
Chordaria flagelliformis	—	—	—	—	—	·7810
Cladophora glomerata (fresh water)	—	—	—	·0227	—	—

A average of 18 specimens.
B " 23 "
C " 5 "
D average of 12 specimens.
E " 4 "
F " 8 "

The Gulf Stream appears to be the carrier of iodine; and the shores on the west coast of Scotland, Ireland, and Brittany, watered by the Gulf Stream, are the principal iodine producing shores. The *Algæ* have furnished the only practicable European source of iodine, and our supplies of raw material are confined to the shores named. The varieties used are the *Laminaria digitata*, or deep-sea tangle, growing on rocks, and always submerged; the *Laminaria saccharina*, or sugar wrack (so called because it is often covered when dry with a sweet effervescence of mannite), growing on sand or loose pebbles, submerged, but in shallow water. These varieties are called drift weeds, because they are thrown up on the coast by storms. The *Fucus serratus*, or black wrack, growing on the rocks close to low water, and longest submerged; the *Fucus nodosus*, or knobbed wrack, growing next to the last, and less submerged; the *Fucus vesiculosus*, or bladder wrack, growing above the last, and the least submerged. These three varieties are called cut weeds, because they are cut from the rocks, as all are exposed at low water. All the varieties are named in the order in which they contain iodine, the first being the highest, as shown in the preceding table. The *Laminaria digitata* is the best source of iodine, and forms the best drift kelp; it is thrown ashore in two parts, the "tangle," or sea rods, are cast up in the winter by violent storms, and the "bardarrig," or tangle top, comes ashore principally in May and September. The former is the stem of the plant, and the latter the frond; both vary in the proportion of iodine, the latter considerably. The following table shows analyses of specimens from different localities:—

	Laminaria digitata.		Laminaria saccharina.	Fucus		
	Tangle.	Bardarrig.		Serratus.	Nodosus.	Vesiculosus.
Ireland—						
Larne,	·418	—	—	·111	—	—
Ballina,	·488	·244	—	·171	—	—
Sligo,	—	·407	—	·111	—	—
Galway,	—	·222	—	·092	—	·059
Clare,	·334	·143	—	—	—	—
Skibereen,	·501	·314	—	—	—	—
Scotland—						
Shetland,	·477	—	—	—	—	—
Stornoway,	·310	·229	—	·107	—	—
Harris,	·435	·178	·331	·059	·037	·021
Vallay,	·431	·142	—	·052	—	·031
Baleshare,	·349	·121	—	·067	·099	—
Boreray,	·509	·198	—	·052	051	·044
Hisker,	·521	·166	—	·079	—	—
Skye,	·498	·262	·518	—	—	—
Tobermory,	·379	·263	—	—	—	—
Coll,	—	·267	—	—	—	—
Tyree,	·445	·249	—	·089	—	—
Colonsay,	·398	·712	—	—	—	—
Strone,	—	·593	—	—	—	·025
Kilcreggan,	—	·445	—	—	—	—
Iona,	—	—	·201	—	—	—
Fife,	·386	·278	—	—	—	—
Dunbar,	·450	·287	—	—	—	—
England—						
Peele,	·679	·338	·189	—	—	·022
Scarborough,	—	·331	—	—	—	—
Worthing,	·478	·267	·158	·038	·042	·009
Weymouth,	—	·259	—	—	—	—
Norway,	—	—	—	—	—	·027
Denmark,	—	·272	—	·104	·128	—

Several of these figures are averages of a large number of analyses. They represent the iodine contained in the kelp-producing *Algæ* collected on different shores, in 100 parts of the dry plants (STANFORD).

The marine animals which yield iodine are :—The common sponge, the horse sponge, *Lapis spongiarum*, *Spongia oculata*, *Flustra foliacea*, various species of *Sertularia* and *Tubularia*, various kinds of *Rhizostoma* and *Cyana*, *Asterias rubens*, *Crogpon vulgaris*, *Mytilus edulis;* oysters contain it, and likewise various species of *Dorus* and *Venus*. It is found in cod-liver oil; and the oil from the liver of the *Raja clavata* and *Raja balis* gives indications of its presence.

DR. DE JONGH estimates the proportion in cod-liver oil as follows :—

Pale oil,	·03740	iodine per cent.
Pale-brown oil,	·04060	" "
Brown oil,	·02950	" "
Average,	·03583	" "

GRAGER estimates it at ·0846 per cent., HOCHENRODEN at ·1620. Even the smallest of these proportions is quite sufficient to make it an important agent in the medical effect of the oil.

STANFORD found it in the curious oil vomited by the Fulmar petrel (*Fulmaris glacialis*) of St. Kilda.

JONAS found traces of it in Scotch salt herrings. Besides these, many other substances of the animal and vegetable kingdom contain small traces of this element. The researches of M. CHATIN have shown that even rain water, dew, air, cider, wine, rose leaves, &c., give very minute traces of iodine.

ZENGER, of Munich, has recently shown that several fresh-water plants contain iodine and bromine in appreciable quantity. He has investigated *Cladophora glomerata* and *Lemna minor*, and even suggests these as sources for manufacturers. The preceding tables, however, show that these plants cannot be compared to the marine *Algæ* as a source of iodine.

Manufacture.—After the discovery of iodine by COURTOIS, he commenced its manufacture. His saltpetre working had become unremunerative. The throwing open of the French ports for foreign products, after the war, brought in immense quantities of saltpetre from India, which at once superseded the old nitre beds, and ruined COURTOIS. In this dilemma he tried to extricate himself by manufacturing iodine; but the consumption of the article being at this time very limited, and the process of its manufacture circuitous, the enterprise was unsuccessful. It was prosecuted, however, by MM. COURNERIE of Cherbourg, in the north-east of France, who were the first manufacturers after the discoverer. With its extended application in medicine, in photography, and in dyeing, others were induced to turn their attention to the subject, and a number of manufacturers followed in France and Britain, especially in Glasgow (which is still the principal seat of the manufacture). Iodine was first made from the kelp liquors by evaporating to dryness, and distilling in an alembic with oil of vitriol, the reaction being—

Sodium Iodide.		Sulphuric Acid.		Sodium Sulphate.		Water.		Sulphurous Acid.		Iodine.
$2NaI$	+	$2H_2SO_4$	=	Na_2SO_4	+	$2H_2O$	+	SO_2	+	$2I$.

This method is not profitable, because the sulphurous acid reacts upon the iodine and water, producing sulphuric acid and hydriodic acid.

Dr. URE made it from the mother liquor of the soap makers using kelp lyes, by saturating with sulphuric acid, and distilling in glass globes with peroxide of manganese. The equation representing the process is as follows :—

Sodium Iodide.		Sulphuric Acid.		Manganese Peroxide.		Sodium Sulphate.		Manganese Sulphate.		Water.		Iodine.
$2NaI$	+	$2H_2SO_4$	+	MnO_2	=	Na_2SO_4	+	$MnSO_4$	+	H_2O	+	$2I$.

The raw material is known as kelp, or varec, as it is called in France; and as the yield of iodine depends entirely on the care taken in the preparation of this crude material, it is necessary to fully describe the means employed.

The manufacture of kelp, or the burning of seaweed to obtain its ash, was commenced about the middle of last century, and was first carried on for the value of the sodium carbonate contained in it; but when the high war duties were taken off foreign barilla and salt, kelp, for which the demand had been very great, deteriorated in value, and was scarcely worth making. The sodium carbonate is never now extracted from this source; the yield was always small, and it is now made entirely from common salt. At the beginning of the present century, during the war, Highland kelp realized from £20 to £22 per ton. Those were palmy days for the Highland proprietors. The small island of Colonsay yielded 200 tons of kelp, or £4000 per annum. The Long Island yielded 4000 tons, and a nett revenue from this source alone, and free of all charges, of about £30.000 per annum. The sum paid to the burner was only 35*s.* per ton. The Hebrides afforded 6000 tons of kelp per annum, which at £20 per ton = £120,000 per annum, and the total produce of Scotland was then 20,000 tons per annum, representing an annual value of £400,000. This amount has never been manufactured since.

The importation of barilla, notwithstanding a high import duty, then became a formidable rival, and for the twenty-two years ending 1822 the average price of kelp was only £10 10*s.* The duty was then taken off barilla, and kelp fell to £8 10*s.* per ton; and in 1823, on the removal of the salt duty, the price fell to £3, and in 1831 to £2 per ton; from this till 1845 it was still used in the soap and glass factories of Glasgow. During this period the manufacture was unremunerative; but the Highland proprietors still encouraged it, as it had become the only means of getting their rents from the poor crofters. In 1845, however, the manufacture of iodine commenced in earnest. It gave a new interest and importance to this industry, and kelp was in demand. The value of iodine rapidly rose from 6*s.* 8*d.* to 40*s.*, at which it was sold during that year. Some of the richer kelps also rose in price to £10 per ton. The imports into Clyde from 1841 to 1876 are appended, with the extraordinary fluctuations in the price of iodine, mostly arising from the operations of speculators on an article of limited supply.

IMPORTS OF KELP INTO CLYDE, YEARS ENDING JUNE 30.

Year.	Tons of Kelp.	Price of Iodine per Lb.	Average.		Fluctuation.	
			Tons.	Price.	Tons.	Price.
1841	2,565	*£0 5 0				
1842	1,887	0 4 8				
1843	1,965	0 6 0	3133	£0 11 9	1887 to 6086	£0 4 8 to £1 11 1
1844	3,263	0 12 0				
1845	6,086	1 11 1				
1846	3,627	1 1 3				
1847	*4,000	*0 11 0				
1848	*4,400	*0 11 0				
1849	4,731	0 11 0				
1850	11,421	0 10 8				
1851	7,320	0 8 8	5811	£0 12 11	3627 to 11,421	£0 8 8 to £1 1 3
1852	5,418	0 15 0				
1853	6,491	0 15 4				
1854	4,679	0 12 0				
1855	5,826	0 13 4				
1856	6,349	0 13 8				
1857	8,641	0 12 4				
1858	8,123	0 10 6				
1859	8,190	0 9 8				
1860	7,754	0 8 6				
1861	9,722	0 7 0	9730	£0 8 10	6349 to 14,018	£0 5 0 to £0 13 0
1862	9,414	0 5 8				
1863	14,018	0 5 0				
1864	11,349	0 8 4				
1865	13,741	0 7 8				
1866	8,858	0 10 0				
1867	8,174	0 12 0				
1868	8,116	0 12 8				
1869	8,978	0 13 0				
1870	9,257	0 12 8				
1871	9,384	0 14 4	9187	£0 15 11½	8116 to 10,923	£0 10 0 to £1 14 8
1872	10,049	1 14 0				
1873	9,449	1 4 8				
1874	10,923	0 15 8				
1875	8,643	0 10 8				

In 1840 1100 tons of kelp, and in 1845 600 tons, were still used in the soap works of Glasgow.

* Estimated.

In 1845 there were only four chemical manufacturers of iodine in and about Glasgow; in the following year there were twenty makers, and of these three worked up the lyes of the soap boilers. There are now only three manufacturers in this country — Messrs. W. and M. PATERSON, of Glasgow, who are the largest, Mr. HUGHES, of Borrowstouness, using kelp, and the North British Chemical Co. of Dalmuir, using sea-weed. Notwithstanding all the fluctuations in price and the very different uses to which the kelp has from time to time been applied, its monetary value is now about the same as it was one hundred years ago.

The total quantity produced on British shores is about 10,000 tons, of which the western islands of Scotland and the Orkneys and Shetlands contribute about one-third, and Ireland about two-thirds. The average value at £4 per ton is £40,000, and the quantity represents about 200,000 tons of wet sea-weed. Kelp from good drift weed should yield from 10 to 15 lbs. per ton of 22½ cwts.; cut weed kelp will yield only 3 to 4 lbs.

M. TISSIER is the principal manufacturer of iodine and salts of potash in France. This gentleman estimates the total annual production of kelp (*soude brute*) in France at 20,000,000 kilos.; this is close upon 20,000 tons, or about double the yield of the kelp shores of Great Britain. M. TISSIER alone, in his work at Conquet, was annually 4,000,000 to 5,000,000 kilos. The following table shows the products annually extracted from this source by the six principal factories in France :—

Works.	Iodine and Iodide of Potassium.	Bromine and Bromide of Potassium.	Chloride of Sodium.	Chloride of Potassium.	Sulphate of Potash.	Nitrate of Potash
	Kilos.	Kilos.	Kilos.	Kilos.	Kilos.	Kilos.
Le Conquet,	20,000	1,500	800,000	500,000	200,000	200,000
Cherbourg,	5,000	—	200,000	180,000	80,000	—
Montsarac,	4,500	—	180,000	150,000	75,000	—
Pont-l'Abbé,	4,000	200	150,000	140,000	70,000	—
Portsall,	4,000	—	150,000	140,000	65,000	—
Quatrevents,	2,500	—	100,000	90,000	50,000	—
	40,000	1,700	1,580,000	1,200,000	540,000	200,000

The manufacture of kelp as carried on in this country is crude and wasteful. The sea-weed is either cut from the rocks for cut weed kelp, or gathered on the shore as thrown up by storms for drift kelp. In either case the weed is spread on the ground to dry, and then burnt in a shallow pit or kiln to an ash; it is then raked up with iron clats into a fused mass, resembling iron slag.

The disadvantages of the present method are principally the following:—

1st. The high temperature developed in burning, by which much of the iodine is volatilized, and some of the potassium salts; the loss of iodine is often more than half that existing in the weed.

2nd. The high temperature also enables the carbon to deoxidise the alkaline sulphates, reducing them to sulphites, hyposulphites, and sulphides. These become concentrated in the mother liquor, remaining after the extraction of the salts, and entailing a large expenditure of oil of vitriol for their reconversion into sulphates. Wallace (in a paper read before the British Association at Aberdeen, September 14, 1859) estimates the cost of extracting all the salts and iodine from kelp at from 25*s.* to 28*s.* per ton, of which from 11*s.* to 13*s.* are expended in oil of vitriol. The importance of this disadvantage is therefore obvious; the addition of the oil of vitriol to the mother liquor sets free large volumes of sulphuretted hydrogen, a noxious gas, very difficult to get rid off, resulting from the decomposition of these sulphur compounds. To such an extent is this deoxidation carried, that kelp prepared from the *Fuci*, which are rich in sulphates, gives off sulphuretted hydrogen on simple solution in water.

3rd. The crude manner in which the weed is burned in a rough pit, or in heaps on the beach, the kelp thus becoming mixed with the earth, sand, or stones, which are often raked into the mass and form adulterations sometimes even to the extent of 50 per cent.

4th. The general neglect of the winter supply, on account of the difficulty of drying the weeds at that season. This consists principally of the deep-sea *Algæ*, torn up by storms; it occurs in the greatest quantity, and is also much the richest in iodine and potassium salts. Yet this is entirely lost to the kelp maker. Even in the summer, during a wet season, large quantities of drift weed collected by the kelpers are rotted by rain and rendered useless for burning.

5th. The entire loss of the heat produced, and the products of combustion.

These evils were first pointed out by M'Crummen in 1847, and the Highland Society's gold medal was awarded to him to mark the importance of the subject. They have been frequently urged since, and are universally admitted; several reforms have, indeed, been proposed. Kemp has suggested a process, which consists in selecting the stems of those *Algæ* which are the richest in iodine, and crushing them; they are then set by in a tank for a few days, and the most soluble salts, including the iodides, extracted by cold water acidified with hydrochloric acid. The solution is then treated with chloride of lime, and the iodine thus set free precipitated by amido-acetate of lead. The cakes of weed left after pressure are dried and used as fuel, the ashes being preserved *on account of the iodine they still retain*, as well as the other salts. This process has not been adopted, probably because the manipulation, down to the burning of the fuel into ashes, is a complicated labour superadded to the ordinary process, and with little advantage, for the ashes have still to be worked for iodine and potash. The crushing of the weeds, and the drying of the crushed cakes, present great practical difficulties, which those who have had any experience in compressing fresh vegetables will fully appreciate. Wallace's suggestion in the paper before referred to is more simple; he states that it is rather given to call attention to the subject than as a perfect process. He wishes to supersede the present fused kelp by a loose charred ash. He recommends the weed to be charred rather than burnt, and as this ash, from its bulk, would be inconvenient for carriage, it should be lixiviated with a small quantity of water, and the solution roughly evaporated to dryness. He says, "By this treatment a very pure salt would be obtained, the iodine would be wholly preserved, while the cost of working would be more than counterbalanced by the saving of vitriol that would be effected by the absence of the sulphur compounds." This idea meets some of the difficulties of the question, but not all; the saving of iodine would to a great extent be effected, it would make just the difference which now exists between the best Highland kelp and that of the Channel Islands, where sea-weed is used as an ordinary fuel; the former a vitreous mass, with more than half the iodine volatilized, the result of igneous fusion, the latter a loose charred ash, the result of slow combustion at a low temperature, and containing much more of the iodine. The difficulty, however, of completely charring on open slabs such a substance as sea-weed is considerable, and the salts resulting from its lixiviation would be coloured by any portion not thoroughly carbonized. All attempts to induce the people to give up the practise of burning to a slag, and adopt the method of stopping the incineration at a point short of this, have hitherto failed. It seems impossible to make them believe that a different kelp from a different weed is now required.

The Society of Arts awarded their silver medal to a research published by Stanford on this subject in 1863; and the following remarks are extracts from this paper (*Soc. Arts Jour.* February 14, 1862). In the following tables, columns 1, 2, 3, 4, and 5, are shown the present kelp-bearing species. *Laminaria digitata* and *Laminaria saccharina* are the general constituents of "drift weed," or *vraic venant* of the Channel Islands and Brittany; 3, 4, and 5, the *Fucus vesiculosus*, *Fucus serratus*, and *Fucus nodosus*, are generally the "cut weed," or *vraic sciê*, of the Channel Islands and Brittany; 6 and 7, the *Zostera*

marina and *Rhodomela pinnastroides*, have not yet been employed in the manufacture of kelp. They are exceedingly common all round the English coast, particularly the south; the latter has received no application, the former is used in stuffing mattresses. It was proposed some time ago as a substitute for cotton, as it contains a small percentage of fibrous cellulose. It has also been used in the manufacture of paper.

The analyses are stated so as to show at a glance the relative value of each weed for commercial purposes. The water is that driven off at 212° Fahr. (100° C.). The organic matter includes the charcoal and everything dissipated in burning. In the analyses of the soluble portion of the ash, the potash and sulphuric acid are stated separately, and the alkaline chlorides indicate the total amount of chlorides of potassium and sodium, supposing the two alkalies existed entirely as chlorides. The kelp is the fused ash obtained in an open porcelain crucible. On the large scale the yield is rather less, generally from 4 to 5 per cent. of the wet weed.

The estimations of iodine were the results of a separate set of experiments, in which the weeds were carefully carbonized in a covered porcelain crucible at a low red heat. The iodides were dissolved from the charcoal with water, and the iodine estimated as iodide of palladium. Thus treated, the weeds were found to yield much more iodine than when burnt, even at the same temperature, in an open vessel. When thoroughly burnt the poorer weeds gave results which could scarcely be appreciated. *Laminaria digitata* gave ·19 per cent., or less than half the yield from the charcoal; ·19 per cent. corresponds to 12·77 lbs. per ton of kelp, and the iodine usually obtained from the best drift kelp made from this weed does not average more than this. The statement of the amount of iodine from the *Laminaria digitata* is the average of three estimations, and to show the amount that ought to be obtained from this species, this corresponds to 32 lbs. of iodine per ton of kelp (20 cwts). Many of the analyses of sea-weeds hitherto published have been performed on different kelps, and as these always contain the ash of several species, little dependence can be placed on them as an index of the relative composition of each species. The plants here experimented on were carefully selected. The amount of iodine will be seen to be exceedingly small in the *Fucus vesiculosus*, and kelp made from that sea-weed alone is valueless. It yields only ·99 lb. per ton, but practically it always contains the ashes of others sufficient to bring it up to about 3 lbs. per ton. SARPHATI estimated the iodine in this species as low as ·001 per cent.

The yield of potash from that common weed, 7, the *Rhodomela*, is large. The soluble ash it yields is very variable in quantity, the fronds being all more or less covered with zoophytes, which largely increase the amount of ash without adding to the soluble portion. The results given are the mean of three analyses.

TABLE I.—WET SEAWEEDS, CENTESIMAL.

Species.	Laminaria digitata.	Laminaria saccharina.	Fucus vesiculosus.	Fucus serratus.	Fucus nodosus.	Zostera marina.	Rhodomela pinnastroides.
Water,	82·000	81·000	71·000	78·500	58·000	82·000	83 000
Organic matter,	12·710	12·920	23·280	16·220	35·030	14·720	12·878
Soluble ash,	4·170	4·810	4·100	3·360	4·880	2 580	2·940
Insoluble ash,	1·120	1·270	1·620	1·920	2·090	·700	1·182
Total,	100·000	100·000	100·000	100·000	100 000	100·000	100·000
Yield of kelp,	5·900	6·600	7·100	6·100	7·630	3·320	6·368

TABLE II.—DRY SEAWEEDS, CENTESIMAL.

Species.	Laminaria digitata.	Laminaria saccharina.	Fucus vesiculosus.	Fucus serratus.	Fucus nodosus.	Zostera marina.	Rhodomela pinnastroides.
Organic matter,	70·112	67·646	80·358	75·079	83·412	81·796	65·748
Soluble ash,	23·560	25·598	14·079	15·859	11·614	14·319	17·297
Insoluble ash,	6·328	6·756	5·563	9·062	4·974	3·885	16·955
Total,	100·000	100·000	100·000	100·000	100·000	100·000	100·000
Yield of kelp,	33 335	35·112	24 381	28·782	18·159	18·444	37·460
COMPOSITION OF THE SOLUBLE ASH.							
Total amount of sulphuric acid,	2·135	1·627	4·165	4·620	2·927	1·498	2·619
Total amount of alkalies expressed as chlorides,	21·526	23·888	11·400	14·396	10·733	13·209	15·910
Total amount of potash,	6·893	8·958	2·043	4·408	2·546	3·940	6·075
Total amount of iodine,	·4788	·1583	·00985	·0382	·0422	·0457	·0378

The peculiar odour developed by the dense smoke of the burning kelp, which in calm weather can be distinctly traced across the sea for thirty miles, led to the investigation of the products of combustion. The sea-weeds were submitted to a low red heat in an iron retort, connected with suitable condensers, and the results are shown in the following tables. The residual charcoal after the salts are washed out is very similar to that from bones, and the products of destructive distillation are more like those of animal than of vegetable tissues. This is remarkable in a body so near the border line of both kingdoms.

TABLE III.—PRODUCTS OBTAINED BY THE DESTRUCTIVE DISTILLATION OF DRY SEAWEEDS, CENTISIMAL.

Species.	Laminaria digitata.	Laminaria saccharina.	Fucus vesiculosus.	Fucus serratus.	Fucus nodosus.	Zostera marina.	Rhodomela pinnastroides.
Charcoal, including ash,	43·750	47·040	38·040	45·450	35·166	43·272	56·610
Tar,	1·861	2·123	3·835	2·474	3·116	·805	1·078
Aqueous portion,	24·509	27·151	31·988	24·978	24·434	25·341	29 931
Gas,	29 880	23·686	26·137	27·098	37·284	30·582	12·381
Total,	100·000	100·000	100·000	100·000	100·000	100·000	100 000
PRODUCTS FROM THE WATER AND TAR.							
Volatile oil,	·707	·708	·989	·825	not estimated.	·312	·319
Paraffin oil,	·698	·796	1·438	·928	1·168	·302	·404
Naphtha, methylic,	·450	·427	·616	·315	not estimated.	·355	·480
Ammonia, or as,	·609	·965	·736	·862	·929	·537	·611
Ammonium sulphate,	2·362	3·713	2·794	3·348	3·606	2·086	2·373
Acetic acid, or as,	·194	·245	·620	·652 }	not estimated.	·181 }	·272
Calcium acetate,	·259	·326	·816	·469 }		·241 }	·363
PRODUCTS FROM THE CHARCOAL.							
Pure charcoal	13·862	14·695	18·398	20·529	18·578	25·068	22·358
Potassium chloride,	10·831	14·104	3·216	6·940	4·008	6·203	9·693
Sodium chloride,	10·695	9·782	8·184	7·456	6·725	7·006	6·217
Insoluble ash,	6·328	6·756	5·563	9·062	4·974	3·885	16 955
Iodine,	·4788	·1582	·00985	·0382	·0422	·0457	·0378

TABLE IV.—PRODUCTS OBTAINED BY THE DESTRUCTIVE DISTILLATION OF DRY SEAWEEDS, PER TON.

Species	Laminaria digitata.	Laminaria saccharina.	Fucus vesiculosus.	Fucus serratus.	Fucus nodosus.	Zostera marina.	Rhodomela pinnastroides.
	Cwts. Lbs	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs	Cwts. Lbs.
Charcoal, including ash,	8 84	9 46	7 68	9 10	7 4	8 73	11 36
Tar,	41·8 lbs.	47·5 lbs.	86 lbs.	55·4 lbs.	69·8 lbs.	18 lbs.	24·1 lbs.
Aqueous portion,	55 galls.	61 galls.	72 galls.	56 galls.	54 galls.	57 galls.	67 galls.
Gas (approximative),	1205 c. ft.	956 c. ft.	1052 c. ft.	1089 c. ft.	1504 c. ft.	1234 c. ft.	500 c. ft.
PRODUCTS FROM THE WATER AND TAR.							
Volatile oil,	253·4 oz.	253·7 oz.	354·5 oz.	295·7 oz.	not estimated.	111·8 oz.	114·3 oz.
Paraffin oil,	250·2 oz.	285·3 oz.	515·4 oz.	332·6 oz.	418·6 oz.	108·2 oz.	144·8 oz.
Naphtha, methylic,	161·3 oz.	153 oz.	220·8 oz.	112·9 oz.	not estimated.	127·2 oz.	172 oz.
Ammonium sulphate	52·9 lbs.	83·2 lbs.	62·6 lbs.	75 lbs.	80·8 lbs.	46·7 lbs.	53·2 lbs.
Calcium acetate,	5·8 lbs.	7·3 lbs.	18·3 lbs.	10·5 lbs.	not estimated.	5·4 lbs.	8·3 lbs.
PRODUCTS FROM THE CHARCOAL.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.	Cwts. Lbs.
Pure charcoal,	2 86	2 105	3 76	4 12	3 80	5 7	4 52
Potassium chloride,	2 19	2 92	0 72	1 43	0 90	1 27	1 105
Sodium chloride,	2 15	1 107	1 71	1 55	1 38	1 44	1 27
Insoluble ash,	1 30	1 39	1 13	1 91	0 111	0 87	3 43
Iodine,	10·72	3·54	·211	·856	·645	1·024	·847

The charcoal is here represented as pure carbon. In practice the residual charcoal, after lixiviation, has the following composition when dry :—

	Laminaria. (ANDERSON.)		Fucus. (PENNY and others.) Average.
Carbon,	52 54	....	70·32
Phosphates,	10·92	....	1·90
Calcium carbonate,	15·56	....	10·25
Magnesium carbonate,	11·34	....	7·92
Calcium sulphate,	—	....	1·93
Alkaline salts,	5·70	....	1·84
Silica,	3·94	....	5·84
	100·00	....	100·00

The carbon contains nitrogen equal to about 2 per cent. of ammonia. The charcoals generally retain also 20 per cent. of water.

The charcoal is extremely porous, and forms an excellent deodorizer and decolorizer. and is the cheapest yet obtained from any source.

This process has been principally carried out on the large scale in the islands of Tyree and of North Uist, in the outer Hebrides, where it has been going on for some years. Considerable capital is required for the erection of works in these distant islands, but the process is now about to be largely extended by the North British Chemical Company. By utilizing the winter supply it affords employment to a large and indigent population when they most need it; and they have enormously benefited where it has been introduced. The produce of iodine from these shores has been more than quadrupled; and the great advantage to the people has been fully set forth by His Grace the Duke of ARGYLL in evidence before the Privy Council.

Lixiviation.—The kelp as it comes into Glasgow occurs in large masses somewhat resembling iron slag; it is first broken up into pieces about the size of road metal; these are then lixiviated in vats heated by steam and worked exhaustively, the same as those used in the lixiviation of black ash (see SODIUM). A liquor is thus obtained of 45° Tw. density; this is evaporated in ordinary hemispherical boiling pans, and the salts which deposit on evaporation are fished out. In Messrs. PATERSON'S works an excellent modification of this is employed, in which the evaporation is effected by steam. The same arrangement is adopted in other chemical works, as in the manufacture of saltpetre, where, as in this instance, the evaporating liquor deposits crystals which have to be removed from the residual

liquor; for the coolers, see IODINE, Plate I., in which Fig. 1 represents a vertical section, and Fig. 2 a ground plan. A A is a cylindrical wrought-iron pan, in which the liquor is placed: it is heated by a coil of steam-piping, B B, B B, running round the interior, in which steam at 60 lbs. pressure is circulating. The contents are continually stirred by a stirrer, C C, driven by gearing, H: the depositing salts are kept in agitation by scrapers, E E E E, and the whole is discharged through the valve, F. The steam escapes through an aperture in the top to the chimney, and the condensed water from the steam coil through an ordinary steam trap. After boiling the liquor for some time it is reduced to a density of 62° T., and a rough potassium sulphate deposits containing 50 to 60 per cent., combined with sodium sulphate and sodium chloride. If ordinary pans are used these salts are fished out into drainers, but with the steam pan the liquor is run out to settle, and after the salt is deposited the supernatant liquor is run off hot into cylindrical coolers of cast iron, and a crop of potassium chloride crystallizes out on cooling. The mother liquor is boiled down again; it then deposits sodium chloride containing carbonate; it is again run out into the coolers, and another crop of potassium chloride is obtained; this is repeated twice or three times, according to the richness of the kelp, and the mother liquor, having a density of about 85° to 95° Tw., containing the iodides and bromides, reserved for further treatment. The salts thus obtained are technically called "muriate" (potassium chloride), 80 to 90 per cent.; "soft sulphate" (potassium sulphate), 50 to 60 per cent.; "kelp salt" (sodium chloride), containing 10 to 12 per cent. of alkali in the form of sodium carbonate. Unless well washed these salts all contain iodine.

In 1859 WALLACE found in samples of

Muriate,	·72	lb. of iodine per ton.
Soft sulphate,	1·21	" "
Kelp salt, unwashed,	3·45	" "

These salts were from cut weed kelp containing only 4 lbs. of iodine per ton; and the analyses show how rich in iodine the products from drift kelp must have been at that time. In making sulphate from the muriate of those days the presence of iodine was often complained of, and was a serious nuisance to the workmen. Iodine manufacturers now do not sell iodine at the price of "muriate."

The "waste sulphur," obtained as a bye product from the mother liquor, is very tenacious of iodine, and unless very carefully washed will contain 10 to 20 lbs. to the ton.

After the removal of the mother liquor from the salts, in addition to the alkaline iodides and bromides, sulphide, sulphite, and hyposulphite of sodium, with considerable quantities of chlorides, are present in the solution, and owing to their solubility cannot be removed. To obtain the iodine the Scotch manufacturers add to the liquid about one-seventh of its volume of sulphuric acid, of 145° Tw. (sp. gr. 1·725), and having agitated the whole, leave it to repose about twenty-four hours. During this period the sulphurous compounds are decomposed, sulphates being produced, whilst the sulphide of hydrogen and sulphurous acid undergo mutual decomposition, and sulphur is precipitated. At the end of this time the liquor is put into an iron still which is adapted to a series of stoneware receivers. A quantity of dry powdered binoxide of manganese is added, and the expulsion of the iodine effected at a temperature bordering on ebullition.

The binoxide of manganese, by acting upon the chlorides present under the influence of the excess of sulphuric acid, liberates chlorine, which in turn displaces the iodine thus:—

FIRST DECOMPOSITION.

Chloride of sodium.		Binoxide of manganese.		Sulphuric acid.	
$2NaCl$	+	MnO_2	+	$2(H_2SO_4)$	=

Sulphate of sodium.		Sulphate of manganese.		Chlorine.		Water.
Na_2SO_4	+	$MnSO_4$	+	$2Cl$	+	$2H_2O$.

SECOND DECOMPOSITION.

Iodide of sodium.		Chorine.		Chloride of sodium.		Iodine.
NaI	+	Cl	=	NaCl	+	I.

The apparatus employed is shown in Fig. 7. The still, A, is a deep pot of thick cast iron of about 300 gallons capacity, set in brick work over a naked fire; it is covered by a framework of malleable iron overlaid with thick lead, B, having an opening at C, and a stopper at D, the chain, E, being used to lift the lid. It is connected by two leaden arms to stoneware "udells," generally about sixteen to twenty, in two series of eight to ten each. These udells have stoppers of stoneware below, shown at F, to allow water containing chlorine and iodine to drain away into the "shute," G, and into the tank, H, from which it is returned to the vats. The bulk of the iodine is found in the central udells. About half the series of udells is shown in the figure.

After charging the still, as already directed, with the liquor, the binoxide of manganese is added, and the temperature raised nearly to boiling; all the orifices and joinings being previously secured with the stoppers and ordinary clay. The iodine passes over, and is collected in flakes in the receivers. The process is examined from time to time by opening the stopper, B, and when the passage of iodine vapours slackens, more manganese, if necessary, is introduced through the aperture, C, and the operation conducted till the whole of the iodine has distilled over.

A number of distillations are worked off before the iodine is cleared from the udells, every added film increasing the density of the iodine by pressing out the liquid. Iodine prepared according to this process is pure and dry, and fit for immediate sale. It may be obtained quite pure by sublimation or by dissolving in alcohol, precipitating by water, and drying the product.

The iodine occasionally contains cyanide of iodine, which occurs in white needles; this generally arises from insufficient use of vitriol. After each distillation is completed the arms from the still are connected with a leaden or earthenware condenser, more manganese oxide is added, and the bromine distilled off.

Fig. I.

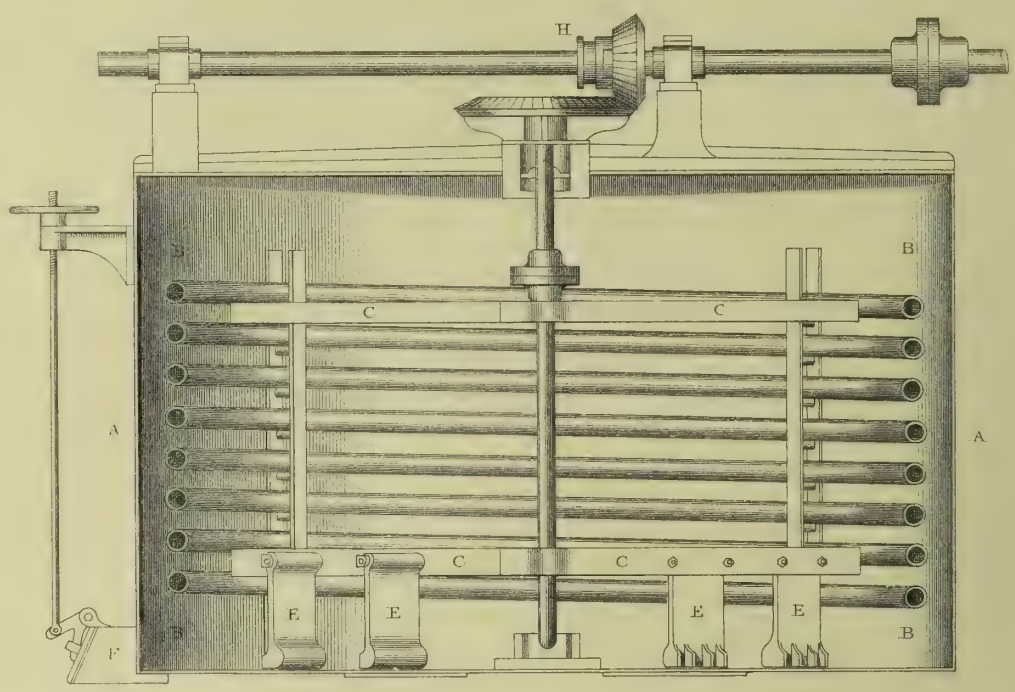
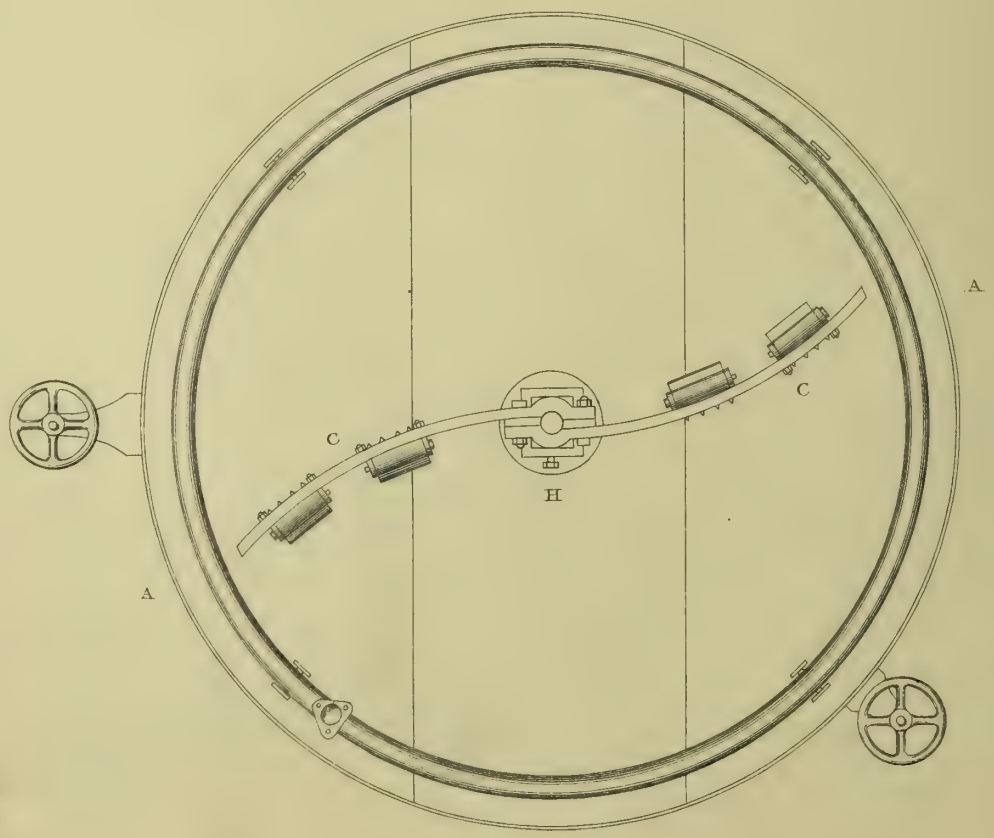


Fig. 2.

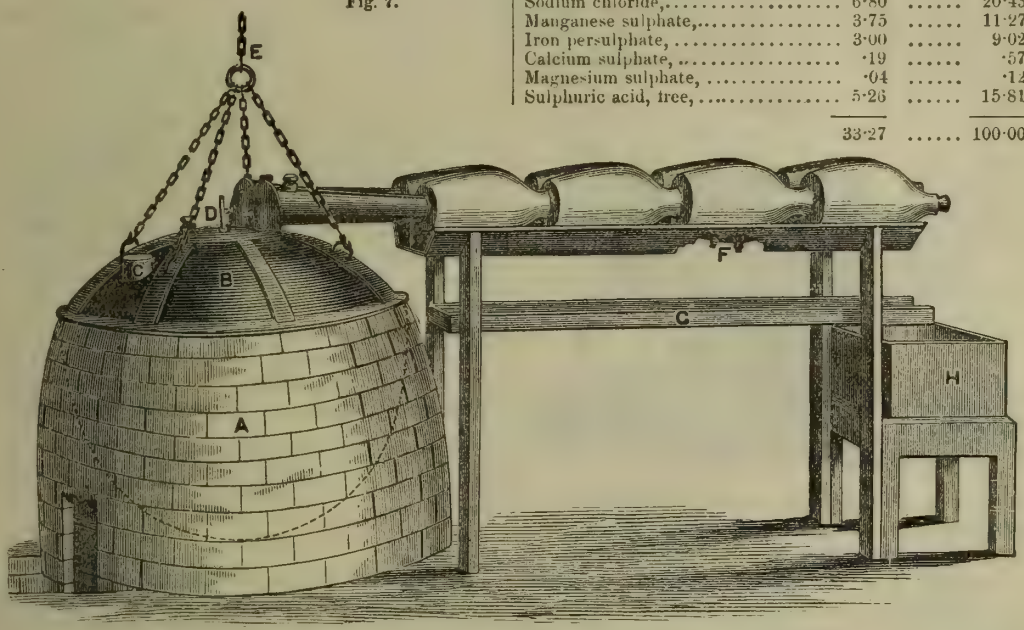


The residual liquor in the still contains traces of iodine as iodides of lead and sodium.

It is known as "waste still liquor;" the composition is shown in the analysis below. The specific gravity varies from 1·235 to 1·5; the amount of dry residue per gallon in the sample tested was 3·327 lbs.

	Liquor. Per Cent.		Dry Residue. Per Cent.
Potassium sulphate,	5·13	.....	15·42
Sodium sulphate,	9·10	.....	27·36
Sodium chloride,	6·80	.....	20·43
Manganese sulphate,	3·75	.....	11·27
Iron persulphate,	3·00	.....	9·02
Calcium sulphate,	·19	.....	·57
Magnesium sulphate,	·04	.....	·12
Sulphuric acid, free,	5·26	.....	15·81
	33·27	.....	100·00

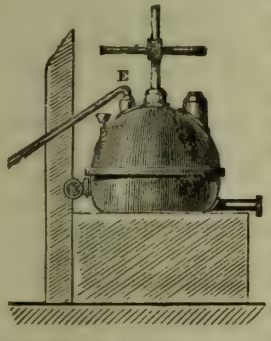
Fig. 7.



It is very troublesome to deal with, and is usually allowed to run away.

In the French works the mother liquors are treated in slight excess with sulphuric acid, and the solution is afterwards boiled for some time; during this operation the sulphides, hyposulphites, and sulphites are decomposed, and sulphur precipitated. Some time is now allowed, in order that the solution may clarify, and when this is effected the supernatant fluid is drawn off from the precipitate, and diluted till it marks 40° Twaddell, and then chlorine is passed into it to saturation from a generating apparatus, such as that shown in Fig. 8. The chlorine passes off from the still, where binoxide of manganese and hydrochloric acid are made to act upon one another, or chloride of sodium, sulphuric acid, and binoxide of manganese, and proceeds by the conduit, E, into the vat, where it liberates the iodine from its combination in the mother liquor. The end of this operation is the decomposition of the iodide present, or rather of the hydriodic acid, and the precipitation of iodine by the substitution of chlorine. In transmitting the chlorine through the liquid, it is necessary to guard against two evils; the first arising from the use of this agent in insufficient quantity, for in this case the iodine compound remains in part undecomposed; the second, produced by an excess of the gas, owing to the formation of chloride of iodine, which passes off in vapour, and is lost. Hence, to determine the exact point, it is necessary to test a part of the liquid as well with chlorine as with a solution of iodide of potassium, to prove, on the one hand, if there remains any further portion of the salt unacted upon, and on the other, if the agent be present in excess. Should the latter be the case, a further addition of mother liquor is made to combine with the free chlorine. When the decomposition is complete, the contents of the vessel are allowed to settle, and after a time the clear liquor containing chlorides and sulphates is drawn off from the iodine. The latter is repeatedly washed by decantation, till the washing gives no indication by the hydrometer of the presence of salts. The iodine is afterwards left to drain in a conical vase of earthenware, the bottom of which is perforated, then dried upon sheets of filtering paper laid upon porous tiles.

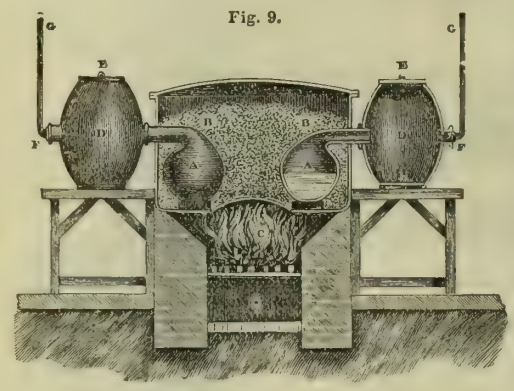
Fig. 8.



The next step is the purification by a process of sublimation in an apparatus like that shown in Fig. 9. The iodine is introduced into the retorts, A A, which form a gallery of two rows, to the number of six; they are immersed in the sand of the cast-iron case, B B, which is heated by the fire, C. Into each of these about 45 lbs. of the crude iodine are introduced; they are then wholly buried in the sand, the neck as well as the body of the retort. This precaution is necessary, to prevent the

condensation of the iodine vapours in the neck, and the obstruction of the passage which would ensue. That this may be guarded against as much as possible, the necks of the retorts are short, and the receivers placed in connection with them as close to the sand-bath as possible. An elliptical cistern, D D, is used for this purpose, the beak of the retort entering at the side. It is furnished with a movable

Fig. 9.



cover, E, to facilitate the removal of the iodine; it has likewise a perforated plate at the bottom, H, to allow any water which may condense to drain off A tubulure, F, at the opposite side to that which receives the beak of the retort, allows the vapour of water to pass off by the pipe, F G, out of the range of the operation. In this way the iodine is obtained in fine large crystals.

When the bromine which is present is to be recovered, the liquor drawn off from the precipitate is evaporated to dryness, the residue mixed with sulphuric acid and binoxide of manganese, and distilled from a leaden vessel. Bromine passes over, and is received in strong sulphuric acid, in which it sinks, and is thus prevented from volatilizing, and injuring the health of the workmen by its fumes.

Another method of separating iodine was proposed by Soubeiran—namely, the addition of sulphate of copper, by which a subiodide of copper is formed. As this only precipitates one-half of the iodine in solution, it is necessary to add ferrous sulphate, when the following reaction takes place :—

$$2NaI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + Na_2SO_4 + Fe_23SO_4.$$

The cupreous iodide is desiccated at a gentle heat, and the dry compound mixed with twice or three times its weight of binoxide of manganese, and as much strong sulphuric acid as will form it into a paste, and the mixture strongly heated in a subliming apparatus, when iodine passes off and is received in appropriate vessels, thus—

Subiodide of copper. Binoxide of manganese. Sulphuric acid.
$$Cu_2I_2 + 2MnO_2 + 4H_2SO_4 +$$
Sulphate of copper. Sulphate of manganese. Iodine.
$$2(CuSO_4) + 2MnSO_4 + I_2 + 4H_2O.$$

The use of sulphuric acid may be dispensed with in the above process, but the heat must be much more elevated when that agent is not employed. In this case the binoxide of manganese is decomposed into sesquioxide of manganese and oxygen, which displaces the iodine combined with the copper, as shown in the annexed equation :—

Subiodide of copper. Binoxide of manganese. Sesquioxide of manganese.
$$Cu_2I_2 + 4MnO_2 = 2Mn_2O_3 +$$
Oxide of copper. Iodine.
$$2CuO + I_2.$$

Various processes, all of which are kept profoundly secret, are employed in the Peruvian works for separating the iodine from the mother liquors of the nitrate of soda. In one the iodine is precipitated as iodide of copper. The iodine exists as iodate of sodium, and requires to be reduced: it is probable that either sulphurous acid or sodium bisulphite is the agent employed. As with the French iodine, it is wet, and requires sublimation. The following shows the analysis of one of the first lots imported from this source; it is now, however, resublimed, and sent over of considerable purity :—

Iodine,	54·0	The salts contained—	
Soluble salts,	22·2	Potash,	2·57
Insoluble,	·8	Sulphuric acid,	1·23
Water,	23·0	Chlorine,	2·19
	100·0		

Improvements Suggested.—Barruel evaporates the mother liquor to dryness; the residue is mixed with about one-tenth of its weight of binoxide of manganese, and then heated to incipient redness, the mixture being kept stirred all the time. The heat is continued till the sulphides and hyposulphites are thoroughly oxidised, which is known by treating a sample of the substance with sulphuric acid, and observing if sulphydric acid be evolved. In this operation the heat should not be raised to such a degree as would cause the evolution of iodine, of which the characteristic violet vapour would be an indication. Water is added to the mass, and the sulphates and iodides are washed out; using only as much water, however, as will afford a solution of 36° Beaumé. Chlorine gas is now passed through the filtrate, and the iodine which is precipitated purified, as described in the preceding method.

Professor Bechi has indicated a process for obtaining iodine from river and other waters containing it in small proportion. He treats the water with a mixture of 1 part of sulphuric acid and 2 of nitric, and passes the acidulated liquor into a tank or vat, having a funnel-shaped bottom, and filled with animal charcoal. The acids have the effect of removing the bases from the iodine, and on transmitting the solution through the charcoal the latter is retained. To remove the iodine from the charcoal, a solution of potash is added. After a while the iodine is taken up, and an iodide of potassium produced. When the solution has been sufficiently completed, water is allowed to flow upon the mass to dissolve the salt, the solution being drained off in another funnel-shaped vessel, which is stopped in the tube part with sponge or other porous material. The liquor is evaporated to dryness, and the iodine

is obtained in the form of iodide and iodate of potassium, from which the iodine may be obtained in the manner already described.

Schönbein has described several substances which decompose the alkaline iodines, and liberate iodine in the dry way. The most remarkable are arsenious acid, chromic acid, sesquioxide of iron, and protoxide of copper; but there is danger in employing the first of these, lest a portion of the poison might be driven off by an increased temperature with the iodine, and thus render its application unsafe as a therapeutic agent. When three parts of potassium bichromate are ground and mixed with two of potassium iodide, and the mixture is submitted to dry distillation in a stoneware retort, the whole of the iodine is set free, leaving in the vessel a greenish mass, which is a mixture of potassium chromate and sesquioxide of chromium.

The iodine which is thus produced is very pure, and no loss either of it or the reagent is experienced; for the chromate, which is a residuary product of the distillation, is a valuable salt, and applicable to many purposes; whilst the green sesquioxide left after washing away the former may be employed as a pigment; or by fusing it with an alkaline nitrate and carbonate, it may be reconverted into a bichromate of the alkali, which may be employed to decompose a fresh portion of iodide.

Iodine is also set free when anhydrous perchloride of iron is mixed with iodide of potassium, even at ordinary temperatures; and on the application of heat it passes off in dense vapours, which may be received in the usual manner. The change of the substances in this instance is due to the reduction of the ferruginous persalt to that of a protosalt; the liberated equivalent of chlorine combining with the potassium, and setting the iodine free.

Persulphate of iron may be advantageously substituted for the perchloride; for when an alkaline iodine is moderately heated with it, dense vapours of iodine are liberated, free from sulphurous acid. Hence, by employing peroxide of iron and iodide of potassium in equivalent proportions, and adding to the mixture three equivalents of sulphuric acid, so diluted as not to be able by itself to liberate iodine, then moderately heating, the whole of the iodine passes over into the receiver, and the residuary matter is composed only of sulphates of potassium and iron.

Combinations.—All the non-metallic elementary bodies, with the exception of fluorine, are capable of entering into combination with iodine, either in single or multiple proportions, and many of these compounds are extremely stable. Like chlorine, iodine combines with hydrogen and oxygen, forming acid compounds, which in their general characteristics are analogous in every respect. With nitrogen and ammonia it affords compounds which are eminently explosive, but with the other simple bodies its combinations offer little interest beyond the precincts of the laboratory. Many of its compounds with the metals are very valuable, as well in medicine as in many branches of industrial art; and to the chemist they are in frequent demand as effective reagents in analysis. Of these, however, reference will be made only to those of the alkaline metals, of iron, silver, mercury, and a few others.

Iodide of Hydrogen—Hydriodic Acid, Iodhydric Acid. — Next to oxygen, chlorine, bromine, and fluorine, iodine manifests the greatest affinity for hydrogen; consequently, it abstracts this element from its combinations of phosphoretted hydrogen, sulphydric acid, ammonia, as well as from alcohol, ether, and volatile oils; in each instance hydriodic acid results. A similar metamorphosis with regard to the iodine takes place when it is mixed with water in the presence of a body capable of abstracting oxygen from the latter; and by this means hydriodic acid is sometimes prepared. Thus, when a mixture of 9 parts of iodine and 1 of phosphorus is introduced into a tube, and covered with moist quartz, sand, or powdered glass, and heat applied, decomposition of iodide of phosphorus, which is at first formed, takes place, as it comes in contact with the thin stratum of moisture, and gaseous hydriodic acid is produced; or amorphous phosphorus may be used; it should be covered with a layer of water, and iodine gradually added. The mixture heated gently in a retort gives off a steady stream of the hydriodic acid gas. Another method is to gently heat in an ordinary flask 1 part of phosphorus, 14 of iodide of potassium, and 20 of iodine, with a little water. When the evolution in this case becomes too rapid, the retort should be cooled by plunging it in cold water:

Potassium Iodide.	Iodine.	Phosphorus.	Water.	Potassium Pyrophosphate.	Hydriodic Acid.
$4KI$	$+ I_{10}$	$+ P_2$	$+ 7H_2O$	$= K_4P_2O_7$	$+ 14HI.$

The gas may be collected over mercury, or condensed in water, forming liquid hydriodic acid.

Other modes may be adopted for preparing this acid dissolved in water; thus, iodide of barium may be decomposed by an equivalent proportion of sulphuric acid, and the liquid, after filtering off the insoluble precipitate of sulphate of barium, concentrated. The usual manufacturing process is to diffuse iodine in water; sulphydric acid is then transmitted through it, when decomposition of the latter takes place, sulphur being precipitated, and hydriodic acid produced. The difficulty in this process is the covering of a portion of the iodine by the depositing sulphur, thus preventing its solution. This loss may be obviated by saturating a given volume of water with iodine, and after allowing the insoluble portion to subside, and decanting the brownish fluid, the sulphydric acid should be passed through it till it becomes colourless. The deposited sulphur is then filtered off, and the filtrate again charged with the iodine, and the portion which dissolves again acted upon as before. In this way the whole of the iodine may be converted into the acid; for at each succeeding saturation, in consequence of the portion of the hydriodic acid that is formed, the liquid acquires the property of dissolving a larger quantity of the iodine. Hydriodic acid may be obtained with considerable facility by

passing the gas through a solution of iodine in alcohol; but it is accompanied by a product of disagreeable odour arising from the action of the sulphydric acid on the alcohol. Naumann operates at first on a small scale, until the reaction is accelerated by the solubility of the iodine in the hydriodic acid produced. The liquid is then cooled, and iodine and water are added from time to time as the action slackens. In this manner a very rapid stream of hydrogen sulphide is completely absorbed, and in a short time large quantities of hydriodic acid are obtained of specific gravity 1·56.

Hydriodic acid, prepared according to the first of these methods, is a colourless gas, soluble in water, and capable of strongly reddening litmus; it has a very pungent odour, somewhat similar to hydrochloric acid. When allowed to escape into the air it produces dense white vapours, which are very suffocating when inhaled. Its specific gravity is 4·4429; it is neither a combustible body nor a supporter of combustion. It may be liquefied by pressure, and solidifies at —51° C. (—59·8° Fahr.). In this state it is perfectly transparent and colourless, but intersected with fissures like ice. The tension of the vapour at 0° is 2·9 atmospheres. Steam, sulphurous acid, chlorine, bromine, and a few other bodies, are capable of decomposing hydriodic acid with the separation of iodine. The gas is composed of equal volumes of iodine vapour and hydrogen, without condensation. In the liquid state hydriodic acid is colourless, and possesses an odour similar to that of the gas. Upon exposure it gradually suffers decomposition, and on prolonged contact with the air oxidation causes the liberation of the iodine, which separates in fine lamellar crystals.

Sulphuric acid, when concentrated, sets free the iodine, forming sulphurous acid and water. It is also decomposed by nitric acid, chlorine, and bromine.

This acid is capable of decomposing the oxides of most of the metals affording metallic iodides and water. The following table shows the relative strength of aqueous hydriodic acid at different specific gravities:—

Specific Gravity at 59° Fahr. (15° C.).	Per Cent. of Acid.
1·708	51·9
1·551	47·2
1·442	39·2
1·297	30·3
1·175	18·5
1·053	5·9

Oxygen Acids.—Iodine forms, with oxygen, compounds of various degrees of oxidation. The best known are iodic acid (HIO_3) and periodic acid (HIO_4). These form salts with the metallic bases, called iodates and periodates, respectively.

With sulphur, phosphorus, chlorine, and bromine, iodine produces several compounds which are very interesting to the chemical student.

Iodide of Nitrogen.—The combination of iodine with nitrogen is remarkable, in being analogous to the chloride of nitrogen, although its explosive properties are much less violent. When iodine is digested with a strong solution of pure ammonia, this compound is precipitated as black powder. The powder should be washed on a filter with water, to remove the excess of ammonia and the iodide of ammonium which forms. Another method is to dissolve the iodine in alcohol, and add excess of strong solution of ammonia. After briskly agitating, the mixture is diluted with water, upon which the iodide of nitrogen precipitates, and may be washed in the cold. The compound is dried carefully upon bibulous paper at the ordinary temperature. In performing this operation, care should be taken to divide the mass into small portions, which ought to be placed at a distance from one another, in order to preclude the possibility of an explosion of any considerable quantity of the salt.

It may be desiccated with safety in a receiver filled with ammoniacal gas.

The slightest agitation will decompose the iodide of nitrogen with a violent explosion, and the evolution of a violet light. The feather of a quill drawn over the powder is sufficient to produce this effect, and if contained in a dish in moderate quantity, the force is such as to shatter it in pieces. Even if rubbed strongly under water, an explosion takes place; but the causes which determine this change in the air are incapable to effect the decomposition when it is mixed with large quantities of water. It is not liable to explode by mere contact with oils and fats, like the chloride of nitrogen. When moist it decomposes slowly in the air, evolving nitrogen, iodic and hydriodic acids. It differs in composition, but all the analyses point to the constitution of an iodamide. NHI_2 and NH_2I have been described.

Iodide of Ammonia (*Iodammonium*, NH_3I).—When dry ammoniacal gas and iodine are brought in contact combination takes place, and a heavy, blackish-brown, very tenacious liquid is produced. The compound is easily decomposed in part when heated, ammonia being set free; the chief portion of the iodine salt, however, sublimes in violet-coloured vapours. It indicates the presence of ammonia and iodine.

Iodide of Ammonium, NH_4I.—The compound which is met with in commerce, and used chiefly in photography, is prepared by neutralizing a solution of ammonia or carbonate of ammonium with hydriodic acid, and evaporating the liquid in a water bath. When the evaporation is conducted carefully under the bell jar of an air pump, the salt crystallizes in cubes and is colourless; but if exposed to the air, it readily deliquesces, and turns brown, owing to a portion of the iodine being set free. It may be prepared likewise by bringing ammoniacal and hydriodic acid gases in contact, or by decomposing iodide of iron by carbonate of ammonia, filtering off the ferruginous precipitate, and evaporating the solution till the iodide crystallizes.

The iodide of ammonium thus prepared is a very deliquescent salt, very soluble in water and alcohol. By keeping, even in diffused daylight when out of contact with air, it decomposes, turning brownish-yellow, ammonia being evolved.

Iodide of Potassium.—When potassium and iodine

are brought together, rapid combination takes place, with a considerable rise of temperature and the evolution of a violet light. The union of the two elements is often attended with a violent explosion. The result is iodide of potassium.

This salt is one of the most valuable compounds of iodine; it is of great importance in medicine; and as a reagent in the laboratory and also in photography it is in general use. There are several methods adopted in its preparation, of which the following are most generally employed:—

Iodine is added to a solution of caustic potassa as long as it dissolves. The point of saturation is known by the liquid acquiring a brownish tint. The excess of iodine is redissolved by a proportionate quantity of the alkaline lye. By evaporation there is obtained a white residuary mass, consisting of iodide and iodate; the latter is decomposed by fusing the mass with a little charcoal, when the iodate is decomposed, and iodide of potassium only remains. The temperature must not be too elevated, or some loss of iodide of potassium by volatilization is sustained. No iodine is liberated, and the whole of the oxygen of the iodate is taken up by the carbon, which is thereby converted into carbonic acid. After heating, the mass is exhausted with water, which dissolves out the iodide. Alcohol may be substituted with advantage when a very pure product is desired, for this takes up only the iodide and leaves the carbonate of potassium, which is nearly always present. By distillation the spirit may be removed, and the iodide crystallized from the concentrated alcoholic solution or from water.

An excellent method is to saturate a solution of carbonate of potassa with hydriodic acid, prepared by the action of sulphydric acid on iodine, and evaporate the solution to crystallization; or it may be made from zinc iodide. Zinc turnings, water, and iodine are agitated together in a close vessel, and the metallic salt which is thus produced is afterwards decomposed by addition of carbonate of potassa to the liquid as long as a precipitate appears. The carbonate of zinc is filtered off, and the solution evaporated to the crystallizing point. The objection to this method is the extreme difficulty experienced in washing out the last traces of iodide of zinc from the precipitated carbonate. In order to obtain a pure salt by this process, Girault gradually pours the cold solution of the iodide of zinc into a boiling hot one of carbonate of potassium as long as there is any effervescence observed; cold water is then added to the mixture, and the whole filtered, and the carbonate of zinc washed twice with water. The trace of zinc still held in solution is removed by the cautious addition of carbonate of potassium, the precipitate filtered, and the liquid concentrated and set by to crystallize. Iodide of iron is more commonly used: 2 parts of iodine, 1 of iron, and 10 of water are agitated together in a close vessel till the liquid loses its brown colour; as soon as this occurs the liquid is filtered, and precipitated by a boiling solution of carbonate of potassium. Care must be taken that the air is as much as possible excluded during the production of the iodide of iron, so as to prevent the formation of a basic iodide of this metal, which could be decomposed only by an excess of alkali.

This process is troublesome on account of the partial solubility of the carbonate of iron in the liquid; this becomes oxidised, and precipitates out during the evaporation.

Iodide of potassium crystallizes from its aqueous solution in the form of cubes, parallelopipeds, pyramids, or octahedrons; and, according to Kane, sometimes in forms belonging to the square prismatic system. The crystals are soluble in about three-fourths of their weight of water at ordinary temperatures, reducing the temperature about 75°·2 Fahr. (24° C.). The boiling point of the saturated solution is about 248° Fahr. (120° C.). It is soluble in less than half its weight of boiling water. It is soluble in 5·5 parts of alcohol of ·850 specific gravity. The salt melts at a temperature below redness, and forms pearly crystals on cooling; if air be admitted to it whilst in a state of fusion, a portion volatilizes undecomposed. Schindler found, when performing the experiment in glass tubes, that the volatilization does not take place below the fusing point of the glass. Chlorine, sulphurous acid, sulphuric and nitric acids, decompose iodide of potassium, yielding iodine in the free state; or in the case of sulphuric acid when diluted, hydriodic acid, as noticed under the manufacture of iodine.

Iodide of potassium may be adulterated with carbonate, chloride, sulphate, and iodate of potassium, and, under particular circumstances, traces of xanthate of potassium. Carbonate of potassium, derived from the imperfect neutralization of the iodide or hydriodic acid, in the first instance, may be discovered by the effervescence which succeeds the addition of hydrochloric acid to a portion of the salt, and also by its solution giving a precipitate with lime water; this impurity remains undissolved when the salt is treated with alcohol. Traces of alkaline chlorides and sulphates may be derived from the carbonate used to prepare the salt. The presence of a chloride is detected by its giving a precipitate with nitrate of silver, soluble in ammonia, and reprecipitated nitric acid. Sulphuric acid is detected by adding to a weak acid solution a few drops of chloride of barium. Alkaline sulphates are also left undissolved by alcohol. Xanthate of potassium is only produced when the iodide is prepared by the action of sulphide of potassium upon iodine dissolved in alcohol. When this body is present the taste of the salt is like that of assafœtida; it turns greyish-brown on being heated, and evolves sulphurous acid; when the heated residue is treated with water, a substance remains undissolved which is composed chiefly of carbon, but traces of sulphates are found in the solution. Iodate of potassium is detected by adding tartaric acid, by which hydriodic acid is liberated; this reacts upon the iodate, its hydrogen combining with the oxygen of the iodic acid of the latter, and setting the iodine free. Thus—

$$HIO_3 + 5HI = 3H_2O + 6I.$$

The change is shown by a brown coloration, but it may be made more delicate by the addition of starch paste, which affords a fine blue tint, even with minute traces of iodate. The disengagement of iodine is indicative of the presence, not only of an iodate, but likewise of any other of the higher oxygen acids. The substances mentioned are seldom contained in greater proportion than 1 to 2 per cent.; chloride is the principal adulteration.

The British Pharmacopœia allows a small percentage of free carbonate, sufficient to give a feebly alkaline reaction, without which the salt does not keep well. The British Pharmacopœia tests are a faint precipitate by saccharated solution of lime, and a yellow precipitate by silver nitrate, insoluble in ammonia, the solution not giving a precipitate with nitric acid. Lead is an occasional impurity, arising from its presence in the iodine; a very small trace of it imparts a yellow tinge to the salt; it may be separated by sulphydric acid.

The iodide should be perfectly soluble in alcohol of 90° to 92°, carbonate, iodate, sulphate, chloride and bromide of potassium all being almost insoluble in this menstruum. Bromide and chloride may be detected by Rose's method. One gram. is mixed with twice its weight of potassium dichromate in powder, and the mixture is introduced into a small flask, having a capacity of 60 or 100 grams.: 2 to 4 grams. of sulphuric acid are added, and the flask immediately closed with a caoutchouc cork, carrying a small tube 10 to 12 centimétres long, and bent at right angles. The flask is heated over a spirit lamp, and the evolved vapours are received in 20 grams. of water containing 3 grams. of ammonia. If there be any chloride present, chlorochromic acid will be formed, and will colour the ammoniacal liquor yellow; if there be only bromine, it will remain colourless.

Bromide of Potassium, a salt now enormously used in medicine as a gentle anodyne, is made in precisely the same way as the corresponding iodide. *Bromide of Ammonium* is also used in medicine, and made as the iodide. These two salts are officinal in the British Pharmacopœia.

Iodide of potassium is used in the laboratory as an important reagent in analysis, and as a means of producing metallic iodides. It is used largely in photography in nearly all the processes employed. It is also used as a precipitant for gold and silver in recovering these precious metals from weak copper ores. The principal use, however, is in medicine, in which it is chiefly employed as the best form of administering iodine.

Iodide of Sodium, NaI.—The description given for the preparation of the preceding iodide will fully answer for the manufacture of this compound. The crystals, however, retain two equivalents of water when they form in an aqueous solution of the salt; they are larger than those of iodide of potassium, and present the appearance of oblique rhombic prisms; they melt in their water of crystallization when heated, giving the anhydrous salt, which dissolves in 0·6 part of water. It is little used.

Iodide of Iron, FeI.—This salt is prepared by agitating water and iron turnings, or fine wire, and iodine together, taking the precaution to retain the presence of an excess of the metal. The iodine attacks the metal, and combines with it, forming a soluble iodide of iron. The compound, though readily prepared in the state of a pale green solution, is more difficult to obtain as a solid, owing to its tendency to decompose, yielding free iodine and a basic iodide, which is but sparingly soluble. During the concentration of the solution of iodide of iron this change occurs, unless it be guarded against by the evaporation being conducted in an iron vessel, or in contact with iron wire, which prevents the oxidation of that portion of the salt which is already formed. Carefully concentrated thus, the compound may be obtained, on cooling, in the state of a green crystalline mass; but it cannot be long preserved if exposed to the air, iodine being set free, and an oxide of iron mixed with iodide remaining. This salt is employed in medicine, principally in the form of syrup, which promotes its preservation; it is also occasionally used as a photographic agent.

Iodides of Mercury.—Mercury forms two important combinations with iodine. If 1 equivalent of mercury and 1 of iodine are triturated together in a mortar, moistening with alcohol, mercurous iodide or green iodide of mercury (Hg_2I_2) is obtained in the form of a greenish powder; the same compound is formed when a solution of mercurous nitrate is precipitated with potassium iodide. If a solution of mercuric chloride, or corrosive sublimate ($HgCl_2$), is added to iodide of potassium, also in solution, a splendid scarlet precipitate of mercuric iodide or red iodide of mercury (HgI_2) is thrown down. If the iodide of potassium has been added only sparingly, the tinge will be duller, in consequence of a portion of chloride of mercury being carried down; on addition of a further quantity of the reagent, however, this is displaced, and the whole of the mercury is converted into the brilliant-coloured precipitate. Too great an excess of the iodide should be avoided, as the precipitate is soluble in iodide of potassium, forming a double iodide of mercury and of potassium.

The red iodide of mercury may be obtained by triturating iodine and the metal together in the ratio of 2 equivalents of iodine to 1 equivalent of mercury, alcohol being added. This, however, should be done with only small portions at a time, for when large quantities are operated upon, the temperature becomes so elevated as to volatilize much of the iodine. A duller-tinted compound is produced in this way than that which results from precipitation.

Both of these iodides may be sublimed in fine crystals. The red iodide is the most stable; it is scarcely soluble in water, but disolves in alcohol, ether, glycerin, fixed oils, and iodide of potassium. When first sublimed the colour is yellow, but on cooling it suddenly resumes its brilliant scarlet tint. This change can be easily seen by spreading the iodide over a sheet of paper and holding it before

the fire. The composition of the salt is unaltered, the change is simply one of physical structure; according to HARRINGTON it arises from rhomboidal crystals being converted into octohedra with a square base.

The red iodide of mercury is used as a pigment under the name of Chinese vermilion.

Iodide of Silver, AgI.—This salt is easily prepared by adding to a solution of silver nitrate hydriodic acid or potassium iodide. It forms a light yellow precipitate, which, when dried and heated, fuses to a reddish liquid mass, changing to a dirty yellow.

The same salt is formed when iodine is made to act upon silver foil, or when concentrated hydriodic acid is poured upon the metal, hydrogen being eliminated. It is found native, as already specified. Iodide of silver is soluble in an excess of the alkaline iodide to some extent, and also in silver nitrate, but is insoluble in water; it is not dissolved by ammonia, which distinguishes it from the chloride. In the presence of moisture, chlorine decomposes the iodide of silver, yielding a chloride of the metal and free iodine, which may be expelled by slightly raising the temperature. This reaction does not take place at a high temperature. M. ST. CLAIRE DEVILLE has shown that hydriodic acid is capable of expelling hydrochloric acid from chloride of silver, and producing an iodide under these conditions; but he also found that on making a mixture of hydrochloric and hydriodic acids, and adding it to a solution of a soluble silver salt, only iodide of silver was produced. Solutions of chlorides of potassium and sodium dissolve iodide of silver freely. Strong nitric and sulphuric acids are capable of liberating iodine from the iodide of silver, a nitrate or sulphate of the metal being formed; this does not occur with the diluted acids.

The chief use which is made of this body is in various processes in photography, in many of which it forms the sensitive medium.

Several other iodides are used in photography to a limited extent, as iodides of magnesium, cadmium, and zinc. Iodide of sulphur and iodide of lead are used in medicine. The former is made by fusing together the two elements in a flask, and the latter by precipitation of lead nitrate by potassium iodide. It is rather soluble in cold water, very soluble in hot water, from which it separates on cooling in brilliant micaceous crystals.

There is a great tendency to the formation of double iodides, and many of these are known.

Estimation of Iodine when uncombined and in combination.—The minute proportion of this element, which has often to be detected in plants, minerals, waters, and even in the air, has taxed the inventive powers and researches of chemists for methods of great delicacy. Fortunately, iodine comports itself with a few bodies in such a characteristic way, offering indications so marked, as not to be surpassed in this respect by any other substance known. These are starch, silver, and palladium; and by proper modifications in the applications of these three reagents, the methods for the estimation of iodine, free or combined, are extremely sensitive and accurate.

Iodine in quantitative determinations is never weighed alone, but in combination with the metals copper, silver, or palladium. In determining the iodine in the cupreous iodide imported from Peru, it is recommended to make 0·8 gram. of powdered zinc into a paste with water, then add 0·5 gram. of the cupreous iodide and more water; metallic copper is thereby precipitated, and the iodine remains combined with the zinc. As a preliminary to the estimation either by silver or palladium, it is necessary to convert the iodine into hydriodic acid or into an alkaline iodide; and for this purpose a sample is weighed, and treated by any of the methods already detailed for the production of hydriodic acid or an alkaline iodide. If the iodine is mixed with potassa, and the brownish liquid treated with sulphide of hydrogen till it becomes colourless, iodide of potassium results; but in adopting this process, the last traces of the sulphide of hydrogen must be expelled, so that they may not interfere with the subsequent precipitation with nitrate of silver. A solution of the latter salt with a little nitric acid is then added as long as any precipitate is formed. By placing the beaker in a warm situation, the yellow iodide of silver falls, and the supernatant clear liquid may be decanted; the residue in the beaker may be washed either by adding water to it, agitating, and after it has subsided pouring off the clear solution, or it may be thrown upon a filter, washed thoroughly, and dried in the water bath. The bulk of the precipitate is detached from the filter and introduced into a porcelain crucible; the paper being burned on the lid at as low a temperature as possible, and the ashes added to the matter in the vessel. Subsequently, the whole is heated to a low red heat, and when cold weighed. From the weight of the substance, minus that of the filter-ash, that of the iodine is calculated—100 parts of iodide of silver being equivalent to 54·128 parts of iodine.

In conducting this operation it is better to wash the precipitate by decantation, and afterwards to transfer it into the crucible, evaporating the water from the latter in the bath, and finally slightly heating over the lamp and weighing. LASSAIGNE'S method of estimation by palladium is still better, and is generally preferred to that just described. It affords a means of determining the iodine in the presence of chlorine and bromine. The liquid containing a weighed portion of the iodide under examination, or of the iodine converted into an iodide or hydriodic acid, is to be slightly acidulated with hydrochloric acid, and a solution of the protochloride of palladium added as long as a precipitate forms; the vessel is then placed in a warm situation for twenty-four hours, at the end of which time the clear liquid is passed through a filter, and the russet-black precipitate collected; it is washed with warm water, and subsequently dried till the weight remains constant, and the iodine calculated from the quantity of palladium iodide thus found.

As it is somewhat difficult and tedious to dry the precipitate when washed with water, some alcohol should be poured on the filter, after all the impurities have been first removed by the hot water. FRESENIUS recommends to exsiccate the compound *in vacuo* over sulphuric acid. As the palladium iodide is decomposed by heat, the weight of the precipitate is taken after expelling the moisture, as above described, the filter being tared and exposed some hours to the heat of a water bath: 100 parts of the dried salt, PdI_2, contain 70·45 parts of iodine. The iodide after desiccation may be heated in the usual way in a platinum or porcelain crucible, and from the weight of the palladium which is left the iodine calculated: 100 parts of palladium are equivalent to 238·5 parts of iodine. LASSAIGNE found that the $\frac{1}{400000}$th part of iodide of potassium could be determined in a liquid by this means, and ZENGER more recently has stated it at $\frac{3}{2000000}$ths.

Upon the reaction of chloride of palladium with hydriodic acid or a soluble iodide, KERSTING has founded a volumetrical method. He prepares for the purpose a number of test liquors with pure iodide of potassium and protochloride of palladium; the iodide of potassium solution is made of such a strength as to contain 1 part of iodine in 1000 of the liquid. This is done by dissolving 13·07 parts of the ignited salt in 10,000 parts of distilled water.

The palladium test liquor is prepared by dissolving 1 part of the metal in nitrohydrochloric acid with the aid of heat, evaporating the solution to dryness in a water-bath, and adding to the residue 50 parts of concentrated hydrochloric acid and 2000 parts of water. The value of this liquid is to be ascertained by adding to a given volume of it the iodide of potassium solution in successive portions, till the whole of the metal is thrown down. If the iodide test liquor be poured from a burette holding 1000 grains of water, and divided into 100 divisions, the amount of palladium in the volume of solution operated upon may be readily ascertained from the number of measures added, since each division contains exactly 0·1 grain of iodine, which is equivalent to 0·0419 of palladium.

Having thus ascertained the quantity of materials in the two test liquors, the iodide to be examined is dissolved in water; a certain measure is then taken and operated upon qualitatively, in order to arrive at a knowledge of the probable quantity of iodine contained in it. For this purpose a number of measures of the palladium liquid is taken in a flask and heated in the water-bath; the measures of the liquid under examination are diluted till the 10 make 100 or 1000 grains. After the palladium solution is warmed, the other is dropped in from the burette in portions, taking care not to add too much at once, and also to shake the flask after each addition. The precipitate readily falls, and by drawing off, by means of a pipette, two portions of the liquid into two tall narrow foot-glasses, and adding to one a few drops from the burette and comparing it with the other, it will be readily ascertained whether the whole of the palladium has been thrown down. If not, a further addition is to be made to the solution in the flask, to which the portions taken out for trial tests must be put, and the whole left for a short time until the precipitate has settled on the water-bath. It is needless to say, that as the precise point is approached the solution of iodide of potassium must be added more sparingly, and, when gained, the two liquids ought to be tested with the iodide of potassium and with the palladium liquor, using the former in one of the test-glasses, and the latter in the other. If no indication is obtained, it is proof that the whole of the palladium has been precipitated. Should, however, an excess of the iodide be added, the operator ought to introduce a few measures of the palladium test, and proceed more carefully in the precipitation till the desired point is attained. From the number of measures of the metallic solution operated upon, it is easy to ascertain the iodine, calculating from the data given in the preceding. A second test may now be performed, employing a given number of measures of the solution containing the iodine, and adding the other test solution till there is no further separation of iodide of palladium, in order to arrive at the true amount of iodine with greater certainty.

If the iodide under examination should be insoluble in water, or not well adapted for immediate solution, on account of admixture with foreign substances, it must be distilled from a small retort with sulphuric acid, diluted with two parts of water. Should the distillate contain free iodine and hydriodic acid, a few drops of starch paste, prepared by boiling 1 part of starch with one-tenth part of strong sulphuric acid in 24 of water, and then sulphurous acid till the blue coloration occasioned by the free iodine and starch disappears, or is on the point of disappearing; on the other hand, if the substance distilled with the acid contains organic matter, causing during the operation an evolution of sulphurous acid, which condenses in the receiver, a few drops of the paste must be introduced, and then a solution of bleaching powder, till a faint bluish tinge begins to appear. This is an indication that the whole of the sulphurous acid has been converted into sulphuric acid; it is necessary, however, to destroy the azure tinge in the liquor by a few drops of solution of the sulphurous acid. After this, the testing with the palladium liquor is proceeded with in the manner detailed.

According to KERSTING, dilute hydrochloric, sulphuric, nitric, phosphoric, and acetic acids, and also the neutral salts of those acids with the alkalies, have no influence upon this method; neither have chloride of calcium or of zinc, acetate of lead, sugar, uric acid, and the distillate of urine with sulphuric acid, alcohol, ether, starch paste, oil of lemons, and bromide of sodium, in the presence of acetic acid. The test is interfered with, however, by the presence of alkaline bromides with free mineral acids, especially upon heating; free alkalies, free chlorine, bromine, iodine, and cyanogen; large quantities of nitric acid at a high temperature, and sulphurous

acid; for all these bodies prevent the precipitation of the iodide of palladium. For free iodine, or iodine in combination with chlorides and bromides, this test is the best that can be employed, but it is not adapted for general use in all circumstances; in the estimation of iodine in kelp or seaweed charcoal, when cyanides are present, it gives very discordant results, and is not at all reliable.

The best method of estimation in these crude raw materials is a simple volumetric process, in which the iodine is set free by a mixture of nitric and sulphuric acids, and the solution shaken with carbon disulphide, which dissolves the liberated iodine with a rich red colour; the depth of colour is compared with standard solutions of potassium iodide treated in the same manner, and the iodine estimated by comparison. In practised hands this simple method is capable of great accuracy, and is very generally available.

Kersting has devised another mode, founded upon the behaviour of mercuric chloride with a metallic iodide, tinged blue by the addition of a little starch paste and bromine water, in which case coloration is perceived as long as any of the iodide remains undecomposed by the mercurial salt, but by the decomposition of the last traces the blueness disappears. A test liquor, containing a certain known weight of mercuric chloride in a given volume, is prepared; the iodide to be examined is dissolved, and the liquor so diluted that it will contain about 1 part of iodine in 1000, being previously blued by a little bromine water and starch paste. By adding the test liquor to this solution, iodide of mercury and chloride of the metal, in combination with the iodide, will be formed; but in consequence of the solutions being so diluted, the mercurial iodide dissolves, and so does not prevent the observation of the blue shade. When this disappears, the number of measures of test liquor required are read off, and from them the iodine is calculated. 100 parts of mercuric chloride are equivalent to 93·7 of iodine. When chlorides and bromides are present, also free mineral acids, acetic acid, and the acetates, the results afforded by this method are not exact.

Penny has published a process for testing the quantity of iodine in iodides, volumetrically, by means of potassium bichromate.

For estimating iodine in kelp which contains sulphur compounds, which interfere with its estimation by Penny's process, Wallace recommends the following process:—500 grains of the pulverized sample are boiled with water, and the solution nearly neutralized with nitric acid, and evaporated to a small bulk. It is then transferred to a platinum capsule, and evaporated to dryness. The residue is fused for a few minutes, when all the sulphur compounds are converted into sulphates without decomposing the iodide. The residue is dissolved in water, filtered, and a solution of silver nitrate is added in small successive portions, until the precipitate finally produced is quite white. Nitric acid is now added in excess, and the precipitate well washed by decantation. The last washing is decanted, and 250 grains measure of the strongest liquid ammonia is added, and the mixture vigorously shaken in a small tightly-corked flask. The digestion is continued for several hours, and the silver iodide is then collected on a small tared filter, and washed first with liquid ammonia and then with hot water, dried, and weighed. The weight of the precipitate × ·1 grain (dissolved by the ammonia), divided by 5, and multiplied by ·54, gives the percentage of iodine in the kelp; and this multiplied by 25·2 gives the number of pounds of iodine per kelp ton of 22½ cwts.

For kelp mother liquors, or "finished ley," the process is modified as follows:—Half a cubic inch of the liquor is nearly neutralized with sulphuric acid, and boiled down to a small bulk, water is added, and the solution filtered to separate sulphur. The solution is evaporated to dryness, the residue fused at a gentle heat, and potassium nitrate added in small portions till the mass is quite white, showing that the sulphur has all been oxidized. The analysis is then conducted as already described. Sufficient ammonia must be used, as the precipitate is bulky. The amount of iodine obtained is multiplied by 3456 to find the quantity in a cubic foot, or by 554 for a gallon.

Tatlock recommends a method founded on the difference in the atomic weights of iodine, bromine, and chlorine. The kelp is digested in hot water, the filtrate and washings are neutralized with hydrochloric acid, and chlorine is passed into the solution. The liquid is then shaken up with one-fourth its volume of carbon bisulphide to dissolve the liberated iodine and bromine. The heavy coloured solution is drawn off by a fine syphon, and shaken up with water and zinc filings, and a solution of zinc iodide and bromide is obtained. The solution is divided into three equal parts, one of which is precipitated with silver nitrate. The second is treated with excess of bromine water, which decomposes the iodide, and then precipitated with silver nitrate, which throws down silver bromide and chloride. The third part is treated with excess of chlorine, which decomposes both the iodide and bromide, and which then gives a precipitate with silver nitrate of silver chloride (*Chemical News*, December 17, 1869).

The following rough process has also been suggested for the separation of chlorides, iodides, and bromides:—The solution is precipitated by silver nitrate; the washed precipitate is treated with 5 per cent. ammonia water; this dissolves the argentic chloride, leaving the argentic bromide and iodide. The argentic chloride is precipitated by nitric acid, and the bromide and iodide treated with 15 per cent. ammonia, which dissolves the bromide, leaving the iodide; the bromide is also precipitated from solution by nitric acid.

Ten grains of pure potassium bichromate are dissolved in about 70 measures of the burette, holding 1000 grains of water, and 30 measures of hydrochloric acid are added. A weighed quantity of the salt to be examined is taken and dissolved in like manner in about 1000 grains of water, and to this the liquor from the burette is added

cautiously till the whole of the iodine is precipitated. This is ascertained by letting a drop from the end of the glass stirrer fall upon another of a freshly-prepared solution of ferrous chloride, mixed with sulphocyanide of potassium, and observing if a red coloration be produced. The bichromate solution is carefully added, stirring after each addition till this result is arrived at, and then the number of measures read off. Knowing that every 10 divisions of the test solution contains 1 grain of the bichromate, and that their quantity effects the liberation of 2·437 grains of iodine from the sample, it is easy to estimate the weight of iodine in the quantity operated upon. This process is not available in the presence of the sulphides, sulphites, hyposulphites, or sulphocyanides, any or all of which may occur in kelp.

BUNSEN'S volumetrical method is an excellent process for estimating iodine in the free state. It is formed on the behaviour of sulphurous acid with iodine, which, in the presence of water, converts the iodine into hydriodic acid:—

Iodine.		Water.		Sulphurous Acid.		Sulphuric Acid.		Hydriodic Acid.
$2I$	+	H_2O	+	SO_2	=	SO_3	+	$2HI$.

This reaction is one among the many that the chemist and manufacturer encounter, and which at first sight appears inconsistent, since the converse can be effected as freely, namely:—

Sulphuric Acid.		Hydriodic Acid.		Iodine.		Sulphurous Acid.		Water.
SO_3	+	$2HI$	=	$2I$	+	SO_2	+	H_2O.

The state in which the substances are presented to one another has a great influence upon the nature of the change, and consequently demands careful study. In this case the one or other of these reactions which result is dependent upon the state of concentration of the materials which are taken to produce the effect. By careful experiments BUNSEN found that the first reaction only is produced when a solution of sulphurous acid, containing 0·04 to 0·05 of real acid, is brought into contact with iodine; hence, when this condition is supplied, 1 equivalent of sulphurous acid is converted into sulphuric acid by 2 equivalents of iodine.

Standard solutions of sulphurous acid, of iodine, of iodide of potassium, and some starch paste, are employed. The iodine test liquor is prepared by dissolving 5 grammes of the purest iodine in a concentrated solution of pure iodide of potassium, in a flask holding 20,000 grains measure. A perfect homogeneousness of the liquid should be effected by agitation, and care taken that it does not show any brown tinge. Each division contains ·0025 of a gramme of iodine.

The sulphurous acid test liquor is prepared by saturating distilled water with sulphurous acid at the common temperature; this liquid should be kept in well-stoppered bottles inverted in water. From 70 to 80 measures of this should be added to every 100 measures of distilled water.

The iodide of potassium test liquor is prepared by dissolving 1 part of pure iodide of potassium in 10 parts water. The starch paste must be fresh.

Before proceeding to operate upon samples of unknown composition, it is requisite to find the relative proportion between the iodine and sulphurous acid solutions; and also what quantity of the respective agents is present in a given volume of them. To effect this it is required, in the first instance, to measure off two burette measures, that is, 200 burette divisions of the diluted sulphurous acid solution, and add thereto 6 or 8 divisions of starch paste; then a solution of the iodine is dropped in from the burette, and the flask agitated till there is a slight excess of the iodine, and the starch acquires in consequence a persistent blue colour.

Operating in this way, and supposing that, to convert the 200 divisions of sulphurous acid into sulphuric, 108 of the iodine liquor were required, it is evident that these numbers will stand in the same relation to one another when the iodine is to be determined, as when it is wished to estimate the sulphurous acid. The next step is to find how much pure iodine is contained in each degree or burette division of the iodine test solution, and likewise its effect upon the sulphurous acid. This is done by weighing off 0·40 gramme of dry and pure potassium bichromate, and treating it in a small retort with concentrated hydrochloric acid, and conducting the evolved chlorine into a solution of iodide of potassium. For this end the bichromate and acid are put into a flask, to which a tubulure and tube are adapted, and secured by passing a tube of caoutchouc over the neck, cork, and portion of the tube; a small glass bulb, with its long neck closed by the blowpipe, is put into the end of the eduction tube, and then introduced into an inverted retort, containing the solution of iodide of potassium. Heat is applied by means of a lamp, and after a few minutes' ebullition of the contents of the flask the whole of the chlorine will have passed over.

There will be liberated from the iodide of potassium, by the chlorine evolved from the quantity of bichromate operated upon, 1·024 of iodine. To the solution containing the mixture of iodine and iodide of potassium, the diluted sulphurous acid liquid must be added from the burette till the brown colour of the fluid has completely disappeared, and the quantity is noted, which for example's sake may be taken at 1600 divisions. It is needless to say that there has been an excess of the acid employed on this occasion, and which is to be determined in the next operation, by introducing a little starch paste, and as much of the standard iodine solution as is requisite to communicate a blue colour to the fluid. If for this purpose 20 divisions of the burette are taken, from the following calculation, founded upon the preceding tests, the value of the solution as to the iodine it contains, and the sulphurous acid it changes into sulphuric, is arrived at. As by the previous experiment it was found that 54 divisions of the iodised solution were necessary to oxidise 200 of the sulphurous acid liquor, it follows that 432 of the former will be required to oxidise

the 1600 measures taken of the latter; but as the experiment shows that the iodine liberated from the iodide of potassium is equivalent to this volume of test liquor, minus the 20 divisions required for the excess—that is, 432 — 20 = 412 divisions, corresponding to 1·024 of iodine—it is evident that each burette division of the iodised test liquor contains ·00248 of a gramme of iodine.

To test the iodine in a sample submitted, a portion is to be weighed off in a flask, and dissolved in iodide of potassium of the strength specified in the foregoing, using about 10 divisions of the burette for each one-tenth of a gramme of the iodine. The dilute sulphurous acid liquor must now be added in measured quantities from the burette, till all colour in the solution disappears; the quantity thus used is noted; a few divisions of starch paste are stirred with the menstruum, and the iodine test liquor carefully dropped in, stirring well after each addition till the blue iodide of starch appears. The volume of sulphurous acid and the number of divisions of the iodised test liquor which are required to oxidise the excess of the acid above what was necessary to convert the iodine in the sample to hydriodic acid being known, it is easy to find, by the following mode of calculation, the proportion of iodine in the sample. Thus, supposing that 1000 divisions of the acid solution were taken in the first instance, and that to oxidise the excess which remained of this, 10 divisions of the iodine liquor were required, it follows that the weight of the sample taken, supposing it a gramme, contained 0·6448 of iodine, and consequently, 64·48 per cent; for, as found by the foregoing experiments, 54 divisions of the iodine liquor were equivalent to the oxidation of 200 of the sulphurous one; hence 200 : 54 :: 1000 : 270, and 270 — 10 = 260 × ·00248 —the amount of iodine in each division—gives 0·6448, as stated.

For the detection of the grosser adulterations of iodine, such as plumbago, oxide of manganese, and sulphide of antimony, a rough estimate may be formed of the amount by heating a weighed sample in a porcelain crucible to redness, till the whole of the iodine is volatilized, and weighing the fixed residue. These substances may also be separated by their insolubility in alcohol.

When small quantities of iodine have to be found in the ashes of plants, in spring or river waters, and other substances where the minutest traces have to be detected, the following methods are recommended:—

PRICE'S method consists in operating upon the solution which is supposed to contain the iodide with hydrochloric acid and starch mucilage, and then adding a few drops of a solution of nitrite of potassium, when a blue coloration from the iodide of starch makes its appearance. The hydrochloric acid liberates hydriodic acid; this body is decomposed by the nitrite, the acid of which is set free by the excess of hydrochloric acid—the hydrogen being converted to water, and the iodine liberated. When much iodide is present the colour of the liquid is dark blue, and appears immediately; but when only a small quantity is contained in the substance operated upon, the shade is lighter, and a few seconds elapse before its appearance. This chemist states that he has detected iodine in a solution containing not more than the $\frac{4}{1000000}$th part of it, and that there is no difficulty in ascertaining the presence of iodine in cod-liver oil, and in the mother-liquor from a few pounds of sea-water, by its aid.

GRANGE directs the transmission of a few bubbles of fuming nitrous acid through the solution to be tested and already impregnated with starch mucilage; the reaction is instantaneous; and when the iodine forms about the $\frac{5}{1000000}$th part of the fluid, a pale rose colour, inclining to violet, is produced. With a $\frac{1}{300000}$th, this chemist asserts that the characteristic blue tint appeared; but when only the $\frac{1}{1000000}$th of iodine is present, he states that no satisfactory results can be attained by this test. Coupling it, however, with another method published by RABOURDIN, founded upon the property of chloroform, of dissolving iodine to a red colour, it can be rendered sufficiently accurate to detect the minutest traces. If a portion of the fluid gives no indication with starch mucilage and nitrous acid, the latter is to be transmitted through the solution till it manifests an acid reaction; a small quantity of chloroform is agitated with it, and then drawn off with a pipette; the reddish colour is removed by the addition of a little potassic hydrate, and the aqueous solution then decanted. The nitrous acid test is then applied, when it does not fail to produce the characteristic blue colour. In this way the $\frac{1}{3000000}$th of iodine is easily detected. Bromides do not interfere with these reactions, as they are not decomposed by the nitrous acid.

M. MORIDE has proposed a substitute for the chloroform in the preceding method, which offers advantages in giving a solution which is more highly coloured than the chloroform becomes under similar circumstances. According to this chemist, wherever iodine is indicated by starch paste, it may be proved also by the employment of benzine more satisfactorily. This agent is rendered more valuable from the fact, that the water which is present, or which may be used to wash it, carries away any bromine or chlorine, thus leaving the iodine isolated.

Chlorine, though capable of setting iodine free from its combinations in aqueous solutions, is now rarely employed to detect iodine, since an excess of the agent converts the iodine into a colourless combination of chloride of this element. Bromine comports itself differently, for although it is capable of liberating it, still none of the iodine is redissolved. DE LUCCA has made this behaviour the basis of a method for the analysis of iodides by means of a standard solution of bromide, coupled with the use of bisulphide of carbon, which takes up the iodine as it is liberated by the bromine liquor. From the volume of the latter which is expended in setting free the whole of the iodine—ascertained by the sulphide of carbon being colourless when drawn off with the pipette—its quantity is found.

Kopp has recommended the following process for the estimation of chlorine, bromine, and iodine in organic compounds: — A combustion tube about 60 c.m. long, and 5 to 6 m.m. in diameter, closed at one end, is filled up to 12 to 18 c.m. with the organic substance mixed with pure ferric oxide. A spiral of fine iron wire 20 to 25 c.m. long is then introduced, and finally the rest of the tube is filled with porous anhydrous crystals of sodium carbonate. The spiral is then first heated, the heating being extended until the ferric oxide is reached; the halogens then given off will be retained by the iron as non-volatile compounds. Should traces of the volatile compounds $FeCl_2$, $FeBr_3$, &c., be present, they will be decomposed by the sodium carbonate. When the combustion is completed the contents of the tube are treated with water, the iron compounds decomposed by sodium carbonate, and the halogens precipitated by silver nitrate from the solution.

Iodine is used very largely in medicine; the following preparations are officinal in the British Pharmacopœia:—*Cadmium iodidum*, *Emplastrum plumbi iodidi*, *Ferri iodidum*, *Hydrargyrum iodidum rubrum*, *Hydrargyrum iodidum viride*, *Linimentum iodi*, *Linimentum potassii iodidi cum sapone*, *Liquor iodi*, *Pilula ferri iodidi*, *Potassii iodidum*, *Sulphuris iodidum*, *Syrupus ferri iodidi*, *Tinctura iodi*, *Unguentum cadmii iodidi*, *Unguentum iodi*, *Unguentum plumbi iodidi*, *Unguentum sulphuris iodidi*, *and Vapor iodi*.

For the detection of iodine in sea water, Sonstadt mixes 200 c.c. with a few drops of slightly alkaline solution of sodium sulphide, and adds 2 or 3 c.c. of a saturated solution of silver acetate, and then about one-fourth its volume of strong hydrochloric acid free from chlorine. The liquid is allowed to rest, filtered, and the precipitate washed with dilute hydrochloric acid, then with water. The filter and precipitate are moistened with solution of sodium hydrate, and heated in a covered crucible to low redness for a few minutes.

After cooling it is dissolved in water, and the filtered solution is strongly acidified with sulphuric acid, and shaken with carbon bisulphide and very dilute chlorine water; the iodine is shown by its red colour. He states that 100 c.c. of sea water will give this reaction.

For quantitative estimation he takes 500 c.c. of sea water; after adding a little solution of arsenious acid in hydrochloric acid, and a little cupric sulphate, he evaporates to dryness, and redissolves in water. The insoluble residue is washed and weighed. The filter is ignited with sodium hydrate, and titrated with very dilute chlorine water and carbon bisulphide.

Iodate of potassium is poisonous, and Melsens has shown that chlorate of potassium should not be given with the iodide, as it decomposes it, forming the iodate, which is very dangerous. It is also largely used in photography; in the original Daguerrotype process it was employed in the free state, and in some form of iodide it enters into the composition of almost all the sensitive films employed, the chief being silver iodide. It was for some time largely used in the manufacture of iodide of ethyl, for the production of Hoffman's aniline green. It is a very portable and useful disinfectant.

IRON.—*Fer*, French; *Eisen*, German; *Ferrum*, Latin. Symbol, Fe. Atomic weight, 56.—*Metallic* iron has probably never been found as a natural product. In Saxony and elsewhere, cases have been recorded of the discovery of masses of brown hematite covering a core of native *metallic* iron; but it is more than probable that the iron core was the production of man, and that the hematite covering was the result of subsequent oxidation. Masses of undoubted meteoric origin are frequently found, in which metallic iron forms the chief constituent, alloyed mainly with nickel (which is probably more nearly allied to iron than any other metal), and often mixed up with earthy matter. The following analyses will give an idea of their composition:—

Locality.	Iron. Per cent.	Nickel. Per cent.	Analyst.
Siberia	96·75	3·25	Proust.
America	97·5	2·5	
Hungary	96·5	3·5	
Bohemia	98·5	1·5	
Eastern Cordilleras	91·41	8·59	Boussingault.
Louisiana	90·02	9·67	Sheppard.

Roberts, the chemist to the Royal Mint, has found that these bodies often contain a large quantity of occluded hydrogen.

As exhibiting the nature of the earthy matter accompanying these curious bodies, the following analysis of a meteorite (by M. Dufrénoy) which fell at Chateau Renard, 12th June, 1844, may be cited:—

Iron	7·7
Nickel	1·55
Silica	30·13
Alumina	3·82
Magnesia	28·13
Lime	0·14
Ferric oxide	29·44
Potash	0·27
Soda	0·86
Sulphur	0·39
Oxide of manganese	trace.

Analysis of so-called "native iron," a meteorite weighing 26 tons, found at Santa Catarina in Brazil, analyzed by M. Damour in the laboratory of M. Boussingault:—

Iron	63·69
Nickel	33·97
Cobalt	1·48
Sulphur	·16
Phosphorus	·05
Carbon	·20
Silicon	·01
	99·56

It is now generally conceded that the mode of extracting iron was not discovered till bronze had been long in use. This would seem to be in accordance with what might be expected from the relative affinities of metals for oxygen. Doubtless the noble metals, which have the least attraction for oxygen and most often occur free in nature, were those first used by the ancients. These would probably be followed by bronze, because copper, which forms

its base, also occurs in the native state, though less frequently. Bronze of varying composition would doubtless be formed during the melting of this native copper, owing to the simultaneous reduction of some of the other metallic oxides accompanying the native metal. In this way it is probable that the ancients discovered the efficacy of fire to extract metals from their earths, and it is feasible to suppose that the more easily reduced metals would be those first extracted. However this may be, it is certain that articles of gold, silver, and bronze occur with great frequency in ancient remains, long before there are any indications of the existence of iron. The recent discoveries of Dr. Schliemann have shown that while the ancient inhabitants of Mycenæ have left ample evidence of their possession of, and great skill in working, gold, silver, and bronze, there is no indication that they were acquainted with iron in the metallic state.

Against this generally adopted opinion I. L. Bell states that it should be borne in mind that the mere absence of iron in buildings of high antiquity does not necessarily imply ignorance of the existence of this metal by those who constructed them. The proneness of iron to oxidation might doubtless obliterate all trace of its having been used long before copper or bronze were much affected by atmospheric influence.

Again, the ores of iron occur in such immense abundance, that it requires no stretch of the imagination to regard the accidental exposure of one or other of the natural products containing the metal to heat in presence of charcoal. The iron would be reduced; and the apparatus necessary for continuing the operation in a systematic way is so simple, that few among the rudest savages are unacquainted with the means of producing the metal in its malleable form.

It would scarcely seem possible that the Egyptians could have erected their mighty pyramids without the aid of iron; but we have no positive evidence upon the point, although it is probable that this wonderful people possessed much knowledge which was lost to succeeding ages.

Dr. Percy says: "That the Assyrians were well acquainted with iron is clearly established by the explorations of Layard, who has enriched the collection of the British Museum with many objects of iron from Nineveh of the highest interest. Among these may be mentioned tools employed for the most ordinary purposes—such as picks, hammers, knives, and saws. There is a saw similar in construction to that now used by carpenters for sawing large pieces of timber across. It was found in the North-west Palace at Nimroud; and it is computed that, while it could not be later in date than 880 B.C., it may have been considerably earlier."

Among the ancient Greeks bronze evidently preceded iron; but many passages in Homer show that iron was common in his time, and that even the art of tempering iron, by plunging the hot tool into cold water, was well known. The Romans were early acquainted with the art of extracting iron, and carried it out on a very large scale. They carried the art with them into the countries which they conquered; and Spain, Elba, and other localities attest the magnitude of their operations by the vastness of the débris which they left behind, in the shape of cinders from their furnaces, &c.

The Britons, even before the time of the Roman invasion, appear to have understood the mode of extraction, and after the Roman occupation numerous ironworks were kept going in and near the Forest of Dean, in Yorkshire, and other parts This is proved by the discovery of many Roman coins buried amongst the large heaps of iron cinders in these districts. The Anglo-Saxons held the workers of iron weapons and armour in high repute. According to "Domesday-Book," Gloucester paid a tribute of ten bars of iron and 100 iron rods for nails, &c., for the use of the navy.

The old enceinte walls of Cardiff Castle, at its south-east corner, where it was 11 feet thick and 30 to 40 feet high, were built upon a heap of iron cinders, without any foundation whatever. Samples of these cinders from under the wall gave the following analysis:—

Ferric oxide,	3·571
Ferrous oxide,	55·928
Alumina,	1·925
Oxide of manganese,	·651
Lime,	2·300
Magnesia,	1·802
Sulphuric acid,	·551
Phosphoric acid,	2·404
Potash,	·061
Soda,	·033
Insoluble residue as under,	30·050
	99·276

INSOLUBLE RESIDUE.

Silica,	27·825
Alumina,	·900
Lime,	1 050
Magnesia,	trace.

Several cavities in the cinders contained adherent portions of charred wood, from which it is highly probable that charcoal was the fuel used for smelting. G. Clark of Dowlais, who minutely examined these cinders in *situ*, considers that the walls built upon them certainly date back to the twelfth century, and without doubt the slag heap upon which they are built would be very much older.

The iron made in these early times was doubtless all malleable, and produced in furnaces of the type used by the natives in India and Central Africa. The date of the discovery of *cast iron* is obscure; but it appears to have been made in the fourteenth century, inasmuch as a cast-iron slab, with an ornamental cross, and the inscription "Pray for the soul of John Collins," occurs in Burwash Church, Sussex, which dates back to this period. Agricola, about the commencement of the fifteenth century, writes thus—"Iron smelted from ironstone is easily fusible, and can be tapped off." Cannons of cast iron appear to have been made by Ralph Hodge in the year 1543. He employed a Frenchman, named Bawd, as assistant; and Thomas Johnson, the son of a servant of Bawd, is reported to have made in and before the

year 1595 "42 cast pieces of great ordnance of iron for the Earl of Cumberland, weighing 6000 lbs. (or 3 tons) a-piece. So important had the iron manufacture become by this time, that Acts of Parliament were promulgated to limit the number of works, in order to prevent the too rapid destruction of timber.

In 1584, the twenty-seventh year of the reign of Elizabeth, an Act was passed for the preservation of timber in Sussex, Surrey, and Kent. This Act sets forth, "that whereas by over-great negligence, or number of ironworks which have been, and yet are, in the wealds of the counties of Sussex, Surrey, and Kent, it is thought that the great quantities of timber which hath been grown in those parts hath been greatly spoiled and wasted, and in a short time will be utterly consumed if some remedy be not provided." And then enacts "that no person, from and after the feast of Easter next, shall erect in any place within the said counties any manner of iron mills, furnace, finary, or blomary, for the working or making of iron or iron metal, other than either upon such old and former bayes or pens, whereupon hath lately been or at the time of the new erection shall be then standing some iron mills, furnace, or hammer, or else in or upon such lands as the party so erecting any such new intended works shall continually furnish the same with a sufficient supply of wood standing and growing upon their own proper soil or land, being to him or them in fee simple, &c."

Up to this time charcoal alone was used as the fuel for iron making; but in 1611 a patent was granted by James I. to Simon Sturtevant for the use of "sea coale," or "pit coale." It is questionable how far Sturtevant really succeeded, and the credit of being the first to successfully use coal (or rather coke) for iron smelting is generally awarded to Dud Dudley, who published an account of his discoveries in his "Metallum Martis," or "Iron made with pit coale," &c., in the year 1665. There appears to be no doubt that Dud Dudley did smelt iron in Worcestershire with coke, and that he thereby made much cheaper iron than his neighbours; but he met with very great difficulties and much opposition. His discovery died with him, and the complete solution of the problem was left for Abraham Darby, of the Colebrook Dale Works, Shropshire, about the year 1735.

While the output of furnaces was small, and charcoal the fuel used, bellows answered sufficiently well for producing the blast; but with the introduction of coke more powerful blowing machinery was needed. Blowing cylinders with pistons were first introduced by Dr. Roebuck at the Carron Ironworks in 1760. Even as early as 1676 the blast furnaces in the Forest of Dean had grown to be about 40 feet high, and 8 to 10 feet wide at the boshes. They were blown by a powerful pair of huge bellows driven by a waterwheel. The pig iron produced was converted into malleable iron in a finery with coal as the fuel.

The introduction of coke for smelting, and of reciprocating pistons for blowing, caused a very great increase in the output of pig iron, and rendered an improvement in the production of malleable iron highly desirable. Up to this time pig iron had been rendered malleable by melting it in an open hearth partly filled with fuel, and exposing the iron as it melted to the highly oxidising influence of the blast of air. The metal was thus gradually decarburized, and the pasty mass taken out with tongs, hammered, reheated, and hammered again, until it assumed the form of bars. Various modifications of the general plan were followed in different localities, but the process was both a slow and a wasteful one, although it produced good iron. With the pressing need for improvement appeared the man destined to inaugurate it. This was Henry Cort, who patented his plans for the use of grooved rolls for rolling in the place of hammering in 1783, and for puddling in 1784. Cort, like many other inventors who have benefited mankind by their discoveries, was ruined in the end; but it is not often that the British Government can be charged with such gross injustice as they exhibited towards poor Cort. Because Cort's partner, Adam Jellicoe, deputy paymaster of the Navy, was found to have defrauded the Government to the extent of £27,000, the patent rights and property of Cort were confiscated, and Cort thereby ruined, notwithstanding that it was subsequently proved that, had the royalties under the patent been properly collected, they would have been sufficient to have paid Jellicoe's debt six times over. The story of Cort's wrongs reads more like a romance than a statement of the acts of public men, and those interested in the matter should refer to the records of the case collected by Dr. Percy. While the merit of bringing the puddling process to a practical success must undoubtedly be awarded to Cort, it should in justice be mentioned that George and Thomas Cranage, of Colebrook Dale, devised and patented, in 1766, a very similiar method of working iron; also that Peter Onions, in 1783, patented, described, and illustrated plans that might certainly have been worked out to a like practical success.

For a number of years no important improvement was made upon Cort's plans for puddling; but in 1818 Samuel Rogers, of Nantyglo, substituted an iron bottom coated over with various substances for the bed of sand used by Cort in the puddling chamber, thereby greatly improving the iron and increasing the output of a furnace. The modification termed "boiling" has been the only change of importance in the puddling process from that date to the present time. The severe labour of the puddler, however, caused many active minds to try to devise means for performing this work by machinery; but although we may now fairly claim that the difficulty has been finally overcome, and that mechanical puddling is a practical success, the credit must be shared by many. Undoubtedly the largest share belongs to Danks, of Cincinatti, but Tooth was one of the first, if not the first, to devise machinery for the purpose, and he had nearly reached the goal; while Menelaus, of Dowlais, rendered valuable service in experimenting upon the subject, and in

recording the experience gained for the guidance of others.

I. L. Bell says that the the invention of Danks was regarded as complete in its character, and accordingly five houses were induced to expend very considerable sums in the erection of forges according to the system which it was supposed had proved entirely successful in the United States. Three out of five works were discontinued after a comparatively short period of trial. The other two firms—viz., Robert Heath of Stoke and Messrs. Hopkins, Gilkes, & Co. of Middlesbrough—have persevered; and after many failures and difficulties, this mode of puddling iron may now be considered as successful. It is perhaps doubtful whether up to this period any great economy has attended the application of mechanical puddling, either by the apparatus of Danks or any other system devised for the supercession of severe human exertion. According to a paper * recently read before the Iron and Steel Institute, there seems, however, good reason for believing that the product is superior in quality to that obtained by common hand puddling.

While these changes were going on in the finished iron manufacture, the production of pig iron also underwent great change. The discovery of black band ironstone, by David Mushet, about the year 1800, gave great impetus to the iron manufacture in Scotland. In 1828 James B. Neilson, of Glasgow, patented the heating of the blast used in the furnace; and so great was the economy effected by the very slight increase of temperature then obtained, that by 1835 nearly every blast furnace in Scotland was blown with hot instead of cold air.

In England the utilization of the waste gases from the tops of blast furnaces was effected subsequently to the introduction of the hot-blast; but our neighbours the French were ahead of us in this matter, and the merit of being pioneer is due to Aubertot, who obtained a patent for his plans in 1811. Bertier published an interesting account of these in 1814. In this country James Palmer Budd was the first to use the waste gases for heating stoves in 1845; but the modern appliance termed cup and cone, now almost universally employed for charging furnaces, and at the same time enabling the gas to be collected and utilized, was first used by George Parry at the Ebbw Vale Works in 1850.

In Scotland and Staffordshire, says I. L. Bell, the great economy due to the application of the waste gases for heating the air and obtaining the necessary power for blowing and other purposes, has made little way. In South Wales, and in the works smelting the Cleveland ironstone, it is universally adopted. In the latter the annual saving of coal by its use may be taken at something like one and a quarter million tons, besides a large economy in wages for firemen and ash wheelers.

The invention of the steam-hammer by J. Nasmyth in 1838, patented in 1842, enabled the manufacturer to deal with much larger masses of iron than had hitherto been possible, and rendered him independent to some extent of water power.

The year 1856 is most memorable, since it heralded the great inventions of Henry Bessemer for converting pig iron into "steel or malleable iron without the use of fuel," of Frederick C. Siemens' regenerative furnace, and of Robert Mushet's addition of molten spiegeleisen to the decarburized Bessemer metal. This latter invention has within the last few years been so developed by the production of ferro-manganese on the large scale, that it has enabled the manufacturer to produce what might almost be regarded as two new metals, viz., the soft malleable steel now used by the Admiralty for ship plates, and a class of steel from which castings can be made that rival the compressed steel of Whitworth for density and strength. The merit of developing these branches of the manufacture is due to the skilful men at the head of the Terre Noire Works in France. The credit due to them is all the greater, inasmuch as their discoveries are not due to fortuitous causes or lucky hits, but have been the result of patient and skilful investigation.

Great economy in blast-furnace yields has resulted from raising the furnaces. The first great step in this direction is due to John Vaughan, who, in rebuilding one of the Middlesborough furnaces in 1864, increased the size from 42 feet high by 13 feet bosh to 75 feet by 16 feet 4 inches, and thereby clearly demonstrated the great saving effected by the increase in height and capacity.

The cause of this saving was at the time experimentally examined into by I. Lowthian Bell in his "Chemical Phenomena of the Blast Furnace," in which this writer assigns his reasons for supposing how far economical working can be promoted by extending the dimensions of the furnace, or by raising the temperature of the blast. At present it may suffice to remark, that in the district where furnaces of large dimensions were first introduced the saving has not been under 10 cwts. of coke per ton of iron.

Combinations of Iron with other Elements—*Iron and Oxygen.*—Iron unites with oxygen in several distinct proportions. The following combinations are well recognized and definite in composition.

Ferrous oxide (FeO), containing 56 parts of iron and 16 of oxygen, or 77·78 per cent. iron and 22·22 per cent. oxygen. It is a powerful base, and absorbs oxygen with great avidity, so that its isolation is somewhat difficult. It is described as black, non-magnetic, and easily burning in air to a higher oxide. Its hydrate or compound with water is easily prepared by adding potash or soda to an aqueous solution of its salts, such as green vitriol, which is the protosulphate of iron (ferrous sulphate), Hydrated ferrous oxide is a white flocculent substance, which in contact with air absorbs oxygen, and turns first green and then red, passing ultimately into ferric oxide. Ferrous oxide never occurs free in nature, but, combined with carbonic acid and

* On the separation of Carbon, Silicon, Sulphur, and Phosphorus from Pig Iron, by I. Lowthian Bell.

mixed up with varying proportions of earthy and sometimes with carbonaceous matter, it forms a very large class of iron ores. It occurs also in combination with silica; but the silicates of iron are rarely used as iron ores.

Ferric Oxide (Fe_2O_3).—This is the most stable oxide of iron. It consists of 112 parts iron and 48 of oxygen, or 70 per cent. iron and 30 per cent. oxygen. It is abundantly diffused through nature, either in the free state (sometimes beautifully crystallized), or combined with water as a hydrate. The anhydrous peroxide forms the basis of a very numerous class of iron ores, termed specular ore, red hematite, micaceous ore, &c. It is distinguished by giving a red or brownish-red streak. Its specific gravity is 5·19 to 5·23. It is infusible, except at the very highest temperature. It is easily reduced to the metallic state when heated with carbon, carbonic oxide, hydrogen, cyanogen, or ammonia. Under favourable circumstances I. L. Bell has shown that this compound loses its oxygen at temperatures as low as 140° C. (284° Fahr.). The reduction of a mass takes place from the outside, and the formation of metallic iron is preceded by that of magnetic oxide, then probably ferrous oxide, and possibly even a suboxide.

Magnetic Oxide (Fe_3O_4) contains 168 iron, 64 oxygen, or 72·4 per cent. iron and 27·59 oxygen. It frequently occurs in nature, and often in well-defined octahedral crystals, having a black or blue-black colour and metallic lustre. It is magnetic, and in mass is often strongly polar. Its specific gravity is 4·98 to 5·2. It is not volatile, but is more fusible than the ferric oxide. It is often produced in metallurgical operations. When clean surfaces of iron are exposed to the action of dry steam at a high temperature, a closely adherent film of this oxide is formed upon the metal by the decomposition of the steam. Professor Barff has lately proposed to make use of this property to form a protective coating over the surface of iron. When iron is heated in the presence of moisture, or in air, a coating of oxide is rapidly formed upon its surface, which is of very variable composition. It is technically termed *scale*, and is the cause of very great waste in the heating of iron during manufacturing operations. Ingots of steel weighing half a ton, and having a sectional area of 12 inches by 12 inches, lose about 3 per cent. of their weight in being raised from cold to a bright red heat, even in a Siemens' furnace, and piles of iron lose considerably more. Ferrous oxide appears to be first formed, then gradually magnetic oxide, and ultimately ferric oxide, when the heating is effected in contact with moist air. *Rust* is hydrated ferric oxide. This is rapidly formed upon the metal when exposed to actual moisture in the air. Pure water perfectly freed from oxygen has no action upon iron at ordinary temperatures, but at high temperatures a slight coating of magnetic oxide appears to be formed, which protects the metal from further corrosion. This has been well demonstrated by the durability of the tubes in the Perkins' boiler. Perkins showed at the meeting of the Mechanical Engineers, June, 1877, portions of tubes from his high pressure boilers, which had been working nearly thirteen years, and were yet in a high state of preservation; while he stated that many sets of his high pressure heating apparatus had been working for forty years with the water originally inclosed, without the iron undergoing decay.

Iron and Sulphur.—Iron forms with sulphur a series of compounds somewhat similar to the oxygen series; but of these only one is important to the iron manufacturer, and this only because it forms a secondary product which has lately been produced in very large quantities, and being a bye product forms a cheap source of iron. This is the bisulphide of iron or iron pyrites (FeS_2). It is found abundantly in nature, and has within recent times become the chief source of sulphuric acid. Certain varieties contain small portions of copper, silver, and gold. After the sulphur has been burnt off, the copper is extracted by a process originally devised by Henderson. There is left behind a moderately pure and rich ferric oxide. It is termed "purple ore" and "blue billy," and is largely used for fettling puddling furnaces. Several attempts have been made to effect its direct reduction, as it occurs as a fine powder, which is difficult to smelt in the blast furnace. Sulphur is one of the worst enemies of the iron and steel worker, as even in quantities so small as ·1 per cent. it causes decided "red shortness" in malleable iron and steel. In pig iron for castings it is not so deleterious, and indeed the Swedes consider that it adds strength to cast metal.

Iron and Phosphorus.—Phosphorus unites very readily with iron, and since most iron ores contain more or less phosphates which are very easy of reduction, the pig iron produced from them is found to contain nearly the whole of this element which existed in the ore or the fuel. It confers fusibility upon cast iron and also brittleness. The fine Berlin castings are made from an iron containing a considerable quantity of phosphorus, which accounts for the sharp and delicate impression the iron takes.

Scotch pig iron generally contains about half (·5) per cent. of phosphorus, and being also highly carburized is well suited for foundry work. The Middlesborough and Northampton pig irons contain from 1 to 1·5, or even more, per cent. phosphorus. Extremely small quantities of phosphorus confer "cold shortness" (that is, brittleness when cold) upon malleable iron and steel: 1 per cent. in steel renders it distinctly brittle, and the effect of even half this quantity can be readily detected mechanically.

While sulphur can to a large extent be removed in the slag by an excess of lime in the blast-furnace charge, no means has yet been discovered of keeping phosphorus out of pig iron; and while the greater part can be removed by efficient puddling, the Bessemer process fails to remove even a trace. It is therefore of the highest importance to select those ores and fuels for making Bessemer pig iron that contain the smallest possible quantity of this deleterious element.

According to some recent experiments described

by Bell, it is the high temperature which prevents any separation of phosphorus from iron in the Bessemer converter; and which also, in a modified degree of intensity, is the cause of this element being only partially expelled during the process of puddling. By moderating the temperature, he found that oxide of iron was capable of almost completely freeing Cleveland pig from its phosphorus, while the carbon was still retained in sufficient quantity to keep the iron in a fluid condition.

Where strength is required in castings, phosphoric pig should be avoided; but a moderate quantity of phosphorus renders the iron so much more fluid, that for all ordinary purposes such iron as the Scotch, or a mixture of Cleveland with less phosphoric brands, is almost universally preferred to the purer hematite irons for foundry work. The soundness of the casting from such pig in some measure compensates for want of strength. In like manner the puddler does not object to a moderate quantity of phosphorus, because it tends to keep his iron fluid, and facilitate the removal of carbon.

Iron and Silicon.—Silicon is never found in nature in a free state, and is very difficult to isolate. Yet it is invariably found in pig iron, and sometimes in very large quantities, even up to 10 per cent. or more. It renders iron brittle, and when present in quantities over about 4 per cent. the pig is technically termed "glazed iron." Such iron is frequently formed when a large excess of fuel is used in the blast furnace, and especially if the charge is siliceous. In some respects silicon resembles carbon, but its oxide, silica (SiO_2), is a solid, while the corresponding oxide of carbon (CO_2) is a gas. This is a point of very great importance in the metallurgy of steel. While the quantity of carbon which iron holds in solution is moderately constant, never exceeding 5 per cent., and usually ranging from 2½ to 4½, the silicon is most variable. The product of a furnace will vary in a few hours 2 or 3 per cent. in its contents of silicon. To the Bessemer steel manufacturer silicon is of the utmost importance, as it is the oxidation of this body which produces the greater part of the heat developed during the "blow;" and while it is necessary to have at least 2 per cent. silicon in the pig that is to be remelted in a cupola, in order to insure the blown metal being fluid enough to cast without setting (or forming a "skull"), anything over 3 per cent. endangers the success of the process, by leaving a variable and unknown quantity of silicon in the metal when all the carbon has been burnt out, and the blow is apparently finished.

Iron and Carbon.—No element is of more consequence in its relations to iron than carbon. It is the only reducing agent capable of effecting the separation of the metal from oxygen, which is at the same time both cheap and abundant. But this is not all, for the metal is capable of uniting with variable quantities of carbon up to about 5 per cent., and the effect of different doses of carbon is most marvellous. While pure iron is weldable, highly malleable, does not sensibly harden when heated and plunged into water, is ductile, and fuses only at extremely high temperatures, the presence of from ½ to 1½ per cent. of carbon lowers the fusing point of the metal, causes it to harden when heated and cooled in water, increases the difficulty of welding, reduces its malleability and ductility, but greatly increases its strength. When the quantity of carbon rises above 2 per cent. the alloy becomes easily fusible, but loses its malleability and ductility almost entirely, and is incapable of being welded. What is still more curious is that the carbon may be present in this higher alloy in two different conditions. So long as the metal is in a molten state the carbon is probably wholly in solution throughout the metal; but as it solidifies, some of the carbon often separates out from the alloy, and would, if time allowed, gradually float to the top; but as solidification takes place rapidly, nearly the whole of this liberated carbon is locked up at the moment of setting between the crystals of metal, from which it can easily be detached by the finger nail. This gives rise to two very different classes of iron, viz., "grey" and "white," and between these two extremes we get the varieties of "forge" and "mottled." If the iron has been fully saturated with carbon, the separation may be so rapid that some of it may even rise to the surface in flakes, and float on the fluid metal. This liberated carbon is termed "kish" by the workmen. The slower the rate of cooling the greater is the separation of carbon; while very rapid cooling may not only prevent the formation of kish, but may so lock up, as it were, all the carbon that the metal remains white. In this state the iron is much harder, and more brittle than it would be if allowed to set slowly and become grey by the liberation of the carbon. It has been customary to term the carbon as it exists in white iron "combined," and that which separates out when the iron cools slowly "uncombined," or graphite. This nomenclature has arisen from the fact that when white iron is dissolved in hydrochloric acid no separation of carbon takes place, but carbonic acid and hydrocarbons are formed, while when grey iron is dissolved, a large portion of the carbon remains unacted upon by the acid.

Another most singular fact in connection with this element is that iron may take up carbon while in the solid state as in cementation; and even the oxide when heated possesses the power of absorbing and decomposing carbonic oxide, and precipitating finely divided carbon through its mass to a very great extent.

Combinations of iron with oxygen, sulphur, and phosphorus may, and undoubtedly do, take place in atomic proportions; but the compounds produced are brittle substances entirely devoid of metallic lustre. No similar compound of iron and carbon is known. On the other hand, iron may contain very considerable quantities of the former elements without losing its metallic lustre, and yet most minute proportions confer extremely marked characters upon the product. When we consider that the proportions of sulphur, phosphorus, carbon, &c., which unite with iron, may rise by infinitely small proportions,

it is a question whether we can recognize any of these *metallic* alloys as definite chemical compounds. It seems far more feasible to regard the union as one of solution. Two views may be held—first, we may suppose that the iron dissolves variable quantities of the elements themselves; second, that the iron holds in solution varying quantities of simple but atomic compounds of the metal with these metalloids. The balance of probabilities appears to be in favour of the first of these hypotheses, but both may hold good. We know that when a No. 1 (grey pig) iron is slowly cooled under slag, a large quantity of carbon or kish separates from the iron, and either floats on the surface or becomes locked up between the crystals as they form during solidification. The writer has shown that this kish, if separated from the mechanically adherent portions of iron, is really pure carbon.

It would appear, according to I. L. Bell, that the condition in which carbon exists in cast iron is determined by temperature; for when white iron is exposed to a high degree of heat, it is changed to grey pig.

Iron appears to possess the power of dissolving so much greater quantities of phosphorus, silicon, and sulphur, that we either never reach the point of saturation, or else they stand in regard to iron just as common salt does to water, being as soluble at one temperature as another. Hence we never find these bodies separating from the iron in a free state, while the separation of carbon is quite common.

If graphitic pig iron be subjected to a heat just barely above its melting point, and in an atmosphere that is very slightly oxidising, the metal, with a certain quantity of carbon and silicon, will liquate away, and leave behind a porous mass of graphite and silica, *of the form of the pig*, but having no tenacity whatever. This is a most curious phenomenon, and has been noticed more than once by G. J. Snelus, when a cupola charged with pig iron has scaffolded, and the charge has had to be drawn out when cooled down.

If grey pig iron is melted at a temperature considerably above its point of fusion, the iron possesses the power of dissolving up the free carbon. On the other hand, if the iron is rich No. 1, and is merely kept molten for some time, as is now done in carrying the iron direct from the blast furnaces to the Bessemer converter, the graphite rises to the surface in such quantities that it may occasionally be collected by the cwt.; but in this state it generally carries off with it particles of iron and slag from which it is difficult to separate it.

Iron is known to alloy with several other metals; but it is most prone to unite with those which are most nearly allied to it in their chemical characteristics. Thus the most common metal that is found alloyed with iron is manganese.

Iron and Manganese.—Manganesian oxides are so often found associated with those of iron, that the alloy of the two metals has long been known. Spathose ores are seldom free from manganese, and in Styria, Siegen, and other districts where these ores are used, the pig iron produced contains a considerable quantity of manganese. Such alloys are generally white, and solidify in large crystals. The facets of these are often an inch or two across, and being very brilliant the Germans gave it the name of spiegeleisen, or looking-glass iron. The oxide of manganese has a great affinity for sulphur, and as some invariably passes into the slag, pig iron containing much manganese rarely contains any sulphur. Hence malleable iron and steel from such pig is also free from this element. The importance of manganese was never known, however, till Mushet discovered its use in the Bessemer process. Since that time the manufacture of a special alloy of iron and manganese has been of growing importance. For a long time, although the alloy first used by Mushet was produced from Brendon Hill (Somerset) ores, the supply of spiegeleisen came from the Siegen district in Germany, where rich manganiferous ores are more plentiful than in England. Within the last six or seven years a large deposit of iron ore, much richer in manganese than the German, has been worked in the south of Spain, and this has afforded the means of increasing the percentage of manganese in the alloy from about 10 per cent. to over 20. The Swedes have also discovered and used an ore rich in manganese, and yielding a similarly high class spiegeleisen, while the Americans have for some years produced the alloy from the mineral Franklinite, after having extracted the zinc. Very early in the history of the Bessemer process Henderson, at the instigation of Bessemer, succeeded in producing a much richer alloy than any yet mentioned, by reducing the spent manganese ores of the bleaching powder manufacturer in a Siemens' furnace; but his process lay dormant for a long time, until the Terre Noire Company, after some years of experimenting, succeeded in producing an alloy containing up to 75 per cent. manganese. They at the same time showed the immense value of this alloy, known in commerce as ferro-manganese, in producing the softer kinds of steel, and now it has become indispensable to the steel manufacturer. The action of manganese will be discussed under the head Steel; but the production of these rich alloys will form a fitting sequel to the manufacture of pig iron. Alloys containing from 5 to 20 per cent. manganese are very fluid; but as the manganese increases beyond this point the fusibility decreases, and the alloys lose their crystalline texture, although they are still brittle. With the increase of manganese in the alloy its magnetism decreases, and this fact has been made use of for determining the percentage of manganese, by powdering the samples and weighing the quantity of each which a given magnet could retain. On comparing the weight with a table deduced from similar experiments upon alloys of known composition, the percentage of manganese can be roughly determined.

Chromium has within the last year or two attracted attention as an alloy with iron. Some pig iron produced from Tasmanian ores, lately introduced into England, contains up to 7 per cent. Cr., while over 10 per cent. chromium has been alloyed with iron in the crucible. Chrome steel is said to be of very

fine quality. There is little doubt that chromium may take the place of manganese to some extent in steel, but there appears to be a difficulty in puddling chrome pig. With 10 per cent. the iron is white and brittle, with an irregular fracture. Chrome steel has a very fine close texture. Chrome iron is almost insoluble in nitro-hydrochloric acid, but soluble in dilute sulphuric.

Titanium.—At one time this element was supposed to alloy with iron, and form a compound having wonderful steely properties; but the general opinion of competent metallurgists at present is that the alloy is of very doubtful existence. Titanium is frequently found in nature, and, according to Riley, is one of the most widely-diffused substances, though in small quantities; but it mostly passes into the slag in the blast furnace, although small quantities may, however, pass into the pig iron. In many respects titanium resembles silicon; and titanic ores, such as ilmenite (which exists in large quantities in Sweden and Norway), may be smelted by treating them in the same way as a highly siliceous ore would be treated—viz., by using a large proportion of lime or other base, to flux off the titanic acid. The iron produced from such ores is dark, close-grained, and free from sulphur and phosphorus; but it is expensive to produce.

Tungsten is another substance which alloys with iron. It appears to hold a somewhat intermediate place between silicon and titanium. Mushet's patent "special" steel is an alloy of iron and tungsten. It possesses the property of hardening after forging without being cooled in water, but is brittle. For certain purposes it is a very useful alloy. It has a high capacity for magnetism.

Ores of Iron.—The following are the chief:—

1. *Red Hematite*, specular ore or iron glance, and micaceous ore, are all varieties of anhydrous ferric oxide. It sometimes occurs nearly pure, as in the kidney ore of Cumberland, the crystals of specular ore of Elba, and the dense massive ore from Missouri and from some of the mines around Lake Superior. It is a most widely diffused and abundant ore of iron, and is found in large quantities in Lancashire, Cumberland, Ayrshire, Glamorganshire, Devon, Cornwall, North Ireland, Spain, parts of Germany, on the shores of Lake Superior, in Missouri, Ohio, Tennessee, and Alabama as red hematite; in Norway, Missouri, and Georgia as micaceous ore; in Elba as specular ore. It varies in specific gravity from 4·5 to 5·3, and is characterized by the deep red streak which its powder gives. It is usually comparatively free from phosphorus and sulphur, and on this account is the ore most frequently used for making Bessemer iron; but this is not always the case, as a sample of red hematite from the North of Spain contains over 3 per cent. phosphoric acid, and amongst some of the Cumberland ores masses of pyrites occasionally occur. It sometimes occurs in veins, often very large, as in Missouri and the Lake Superior district; sometimes in enormous pockets in the limestone, as in Cumberland and Lancashire; and occasionally forms a true bedded deposit, as in Alabama, where it lies in a bed over 100 feet thick above the Devonian limestone and below the coal, dipping at an angle of about 10°, and extending over miles of country. Its mode of formation in Cumberland and Lancashire is a disputed point, but the most generally accepted theory is that it was deposited from suspension in water. There are some indications of its having been precipitated from solution in particular cases. Many instances have been noticed where the deposit is evidently a drift material, possibly the accumulation of the denuded veins of older deposits. G. J. Snelus possesses a curious specimen from Missouri, showing the passage of spathose into specular ore. This would probably be due to the action of intense heat accompanied by oxidation. In the Cumberland district in the vicinity of the ore deposits, cases are very numerous where the oxide of iron passes into and appears to saturate the adjacent limestone or sandstone, giving rise to the idea that the iron had been in solution, and had permeated the adjacent rocks and there been precipitated. Red sandstone contains a notable quantity of ferric oxide, apparently precipitated in this impalpable form; and it is a curious fact that in Cumberland the best deposits of ore are generally found where the limestone and red sandstone are contiguous. In the Cumberland district the deposits are classified as hard and soft ores, the former occurring in rocky masses impregnated with veins of carbonate of lime and crystals of quartz; the latter forming deposits of fine soft earthy material, often very unctuous to the touch and very rich. Further south the Lancashire deposits are mostly of this soft earthy kind, and generally contain more oxide of manganese and silica than the Cumberland ores. These ores being dense and impervious to gas are not easy of reduction, but being generally very rich can be smelted with a comparatively small quantity of fuel (see Table I.).

2. *Magnetite, or Magnetic Ore*, often occurs crystallized in beautiful octohedra. It is also an abundant ore most widely diffused, and generally occurs in veins, but sometimes in enormous quantities like sand, as in Canada and New Zealand. These sands are generally titaniferous. The massive ore occurs in Yorkshire, North Wales, Devonshire, Norway, Sweden, Lapland, Russia, France, Germany, Spain, Portugal, Italy, Greece, north coast of Africa, New Jersey, district of Lake Superior, Mexico, Brazil, Australia, New Zealand, Northern India. It is not plentiful in England, but is the principal ore of Norway, Sweden, Russia, New Jersey, and India. It is a dense, iron-black ore, magnetic and often highly polar, the crystals possessing semi-metallic lustre. Specific gravity, 4·9 to 5·2. It is generally more difficult of reduction than ferric oxide, being even less porous, though when composed of masses of aggregated small crystals, as is the case with the Marbella ore, it disintegrates under the influence of heat and a reducing atmosphere. It sometimes occurs free from sulphur and phosphorus, but often contains a large excess of phosphoric acid, and is frequently mixed with iron pyrites (see Table II.).

TABLE I.—RED HEMATITES.

	From Ulverstone, England.	From Restormel Co., Plymouth, England.	From Clifford dist., Cumberland, England.	From Cleator dist., Whitehaven, Cumberland, England.	From Rivadesella, Spain.	Specular Ore from Rio Tinto, Island of Elba.	From Llantrissant, Glamorgan, S. Wales, aver. of 30 samples.	From Clifton, Cumberland, average of 38 samples, England.	From Silter & Eskett, Cumberland, av. of 50 samples, England.	Fr. Millom dist., Cumberland, Hodbarrow Co., av. of 78 samples, Eng.	From a deposit 120 ft. thick near Kirkoy Mog, Christian Gyvern-ment, South Russia.	Lisseer Ore from Klina Mwnyer Foundworks, Hungary.	From the upper parts of the deposit at Iron Mountain, Missouri, United States, America.	From the deeper parts of the deposit at Iron Mountain, Missouri, United States, America.	Pilot Knob, from below the Slate, Missouri.	Shepherd Mountain, Missouri.	Central district of Missouri, Meramec Bank.	Clinton dist., Oneida County, New York, U.S., America.	Geo. McKee's Bank, Mifflin County, Pennsylvania, U.S.	Blacklog Gap, Hunting-don County, Pennsylvania, U.S.	From Region of Chat-tanooga, Tennessee, United States.	Red Mountain, Missouri, United States.	Specular Ore, Jackson Mine, Lake Superior, North America.	Average of Lake Superior Specular Ores, Brooks.	Average of L. Superior Loose Hematites.	Red Hematite, Picton County, Nova Scotia, North America.
Ferric oxide	74·230	60·085	85·461	85·571	83·180	87·840	70·850	80·142	82·285	85·571	68·040	66·060	95·420	91·470	84·330	88·630	85·95	57·880	72·43	81·260	93·750	90·520	75·75	56·06
Ferrous oxide	—	—	—	—	—	—	—	—	—	—	—	1·100	850	76	150	2·970	77	·600	·09	—	—	—	80	9·20
Manganese dioxide	·276	4·537	·055	·186	—	—	—	·186	—	·186	·500	3·490	—	—	—	—	—	—	27	trace.	trace.	trace.	—	—
Manganous oxide	—	—	—	—	—	—	·200	—	—	—	—	—	·090	·150	—	—	—	—	—	—	—	—	—	—
Alumina	6·614	8·495	3·047	1·250	2·630	3·470	1·610	2·030	3·062	—	3·000	2·270	·790	·080	2·190	2·010	2·300	·120	7·84	3·400	4·140	1·390	1·535	5·59
Lime	1·00	·500	·904	1·000	2·700	·220	2·020	1·000	—	·198	1·470	·630	·170	·460	·210	·470	·120	·160	·45	1·600	1·030	·610	·360	1·88
Magnesia	·005	trace	—	·198	trace.	·180	·340	·060	·098	trace.	·065	—	·140	·230	·140	·090	·190	1·080	·74	·500	·340	·230	·420	2·90	1·05
Potash	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica	8·620	18·850	7·400	9·425	10·525	14·370	3·500	5·950	15·185	2·200	22·100	—	1·570	4·750	3·990	13·270	5·987	24·400	41·51	17·00	6·50	31·630	3·270	5·892	14·04	23·68
Carbonic acid	·790	—	—	2·100	1·110	·600	·042	·015	—	—	—	—	—	—	—	—	—	—	—	—	1·50	—	—	—	—	—
Phosphoric acid	·014	·170	·022	·052	·082	—	—	—	—	—	—	·430	·071	—	·252	·035	·390	·480	·547	·281	1·450	·420	·151	·258	·185	none.
Phosphorus	—	—	—	—	—	·010	—	—	—	—	—	·210	—	—	—	—	—	·116	—	—	—	—	—	—	—	—
Sulphuric acid	—	—	—	—	—	—	·427	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sulphur	·019	·076	·074	·055	·020	·170	—	—	·144	—	—	—	·005	—	—	—	—	·126	—	trace.	trace	·030	·050	·110	none.
Titanic acid	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Water	8·432	*6·100	*3·100	1·234	2·204	1·910	8·110	1·463	2·204	—	6·000	8·410	—	—	—	—	—	·46	8·05	5·50	·462	4·00	—	1·090	·770	6·93	2·54
Organic matter	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total	100·000	100·133	100·033	99·169	99·461	100·671	100·49	100·000	1·000	99·610	99·64	100·356	100·016	100·035	100·325	100·340	100·292	99·08	99·659	99·561	100·21	100·000	99·861	100·000	100·000	100·0 0
Total metallic iron	51·92	4·69	59·82	58·50	57·64	56·10	49·60	58·23	57·64	58·50	47·90	47·90	67·42	66·05	59·15	64·310	66·66	40·50	50·70	56·83	43·71	65·62	63·36	53·02	43·40
Average moisture	—	—	4·86	5·55	5·80	4·86	6·44	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Iron in natural ore	—	—	53·37	55·25	54·25	53·37	46·40	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

TABLE II.—MAGNETIC ORE.

	Magnetic Ore from N. Wales.	Magnetic from Devonshire, England.	Magnetic from Wickenridge, Cornwall, England.	Lisbon, fr. Palmer, Hall, & Co. (Magnetic), Spain.	Marbella, Magnetic, South Spain.	From Valley of La Palmitera, near Malaga, Spain.	San Leone, near Gallura, Sardinia, Italy.	Flodberg, Central Sweden.	Lobnia, to the west of River Wurgunum, Chenda dist. of Madras, India.	Average of Lake Superior Magnetic Ores, North America.	Champion Mine, Lake Superior, N. America.	Crown Point, L. Champlain district, North America.	From the celebrated Cornwall deposit, Lebanon Co., Penn-sylvania, U.S.	Carter County, Tennessee, United States.	New Bed, Port Henry, New Jersey, United States.	Stourbridge Mine, Morris County, New Jersey, U.S.	Hewitt Mine, Ringwood, Passaic County, New Jersey, United States.	Cooper Mine, Ringwood, Passaic County, N. Jersey, U.S.	Magnetic Ore from Victoria County, Toronto, North America.
Ferric oxide	25·571	53·070	63·110	56·970	66·14	68·040	62·000	59·424*	69·08*	67·760	74·930	59·750	78·280	93·39	64·980	63 04	69 64	62·11	58 35
Ferrous oxide	33·557	24·930	16·210	16·580	23·14	21·370	24·000	22·638†	29·376†	19·640	17·870	26·30	—	—	30 180	—	—	—	24 87
Manganese dioxide	—	—	—	1·654	trace.	1·400	·800	·174	·090	·110	·050	—	—	·27	—	—	15	·20	—
Manganous oxide	·465	trace.	—	—	—	—	—	—	—	—	—	·280	—	—	·170	—	—	—	·13
Alumina	7·880	—	3·149	1·927	·800	3·420	—	5·481	—	2·130	1·150	1·520	—	·41	2·960	3·87	9·17	2·80	·42
Lime	3·250	·660	1·100	2·450	1·900	2·200	—	·729	·651	·480	·520	·300	1·000	·41	—	3 25	—	6·62	1 43
Magnesia	·540	·450	trace.	5·472	1·360	1·180	—	·058	trace.	·080	·920	·120	1·290	·35	1·470	·86	trace.	·28	2 56
Potash	none.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Silica	16·925	19·200	14·750	8·120	6 100	2·60	—	11·842	·823	7·830	3·700	11 600	11·080	4·68	1·10	6·70	17·50	3·10	11·18
Carbonic acid	·600	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Phosphoric acid	3·561	·300	·071	trace.	trace.	—	—	·003	—	·199	·192	·080	·072	trace.	·190	1·92	·19	5·12	·17
Phosphorus	—	—	—	—	—	·01	—	—	·005	—	—	—	—	—	—	—	—	—	—
Sulphuric acid	—	—	—	—	—	—	—	—	—	—	—	—	·039	—	—	—	4 54	—	—
Sulphur	·510	·110	·211	·016	—	·04	·200	·151	·012	·131	·120	·030	5·222‡	—	·120	·10	—	—	·04
Titanic acid	—	—	—	—	—	—	—	—	—	—	—	—	2·392‖	—	—	—	—	—	·73
Water	6·000	1·560	·900	6·841¶	—	1·74	13·000	—	—	·810	·520	—	·625	·49	—	·70	—	—	—
Organic matter	1·250	—	—	—	—	—	—	—	—	—	—	—	·300	—	—	—	—	—	—
Total	100·029	100·220	99·601	100·000	99·44	100·000	100·000	100·000	100·000	99·990	99·972	99·91	100·300	100·00	100·00	100 44	100·99	100·23	99·88
Total metallic iron	4·400	56·55	55 67	52·77	64·30	64·25	62·06	59·424	69·208	62·93	66·040	62·23	59·23	67·63	68·96	60·13	50·69	59·19	—

a NaO 370. *b* + Co_2. * Iron. † Oxygen. ‡ Sulphide of iron. § Sulphide and oxide of copper. ‖ Oxide of cobalt. ¶ + Co_2.

TABLE III.—BROWN HEMATITE.

	Northampton, Towcester; Calcined, England.	Northampton, Towcester; Raw, England.	Northampton, England.	Northamp., Woodford, average of 220 Samples, England.	Northamp., Green Interior of Lumps, England.	From Forest of Dean, average of 160 Samples, England.	From the Inferior and Great Oolite in the Ardennes, near Virieux, France.	Santander, average of 37 cargoes, Spain.	Bilbao, Sommorostro, Camyanil, average of 300 cargoes, Spain.	Pequena, Spain.	Porman, Spain.	Porman, Spain.	From Rasthoderitze, at Leogang, Austria.	Brown Ore from Eisenerts, Styria, Austria.	Minettes from the Oolite, Luxemburg, Austria.	From very large Deposit on River Sukegaue, South Russia.	From the Island Seriphos, Grecian Archipelago.	Limonite Picton Co., Nova Scotia.	Greenup Co., Kentucky, United States.	Bloomfield, Pennsylvania, United States.
Ferric oxide,	61·34	64·629	62·774	62·142	21·400	51·984	72·420	79·285	78·426	75·47	71·730	76·810	54·13	75 08	61·12	73·40	80 64	93·09	68 93	78 63
Ferrous oxide,	—	—	—	—	30·150	—	—	—	—	—	—	—	—	—	—	—	·96	—	—	—
Manganese dioxide,	trace.	—	—	·325	·208	—	—	—	—	trace.	—	·630	—	·80	·05	1·30	98	1·10	·29	·43
Manganous oxide,	—	—	—	—	—	—	—	·465	1·303	—	·650	—	3·16	—	—	—	—	—	—	—
Alumina,	8·54	3·916	8 926	5·450	7·960	2·859	1·600	·310	1·130	3·70	3·020	4·090	6·72	—	5·30	2·25	1·20	—	2·77	2 50
Lime,	3·90	·900	4 500	1·600	1·840	1·306	·400	·300	3·550	trace.	} 7·580 ₰	{ 2·900	·50	·56	7 04	—	1 90	·91	·68	·34
Magnesia,	trace.	·252	trace.	trace.	·936	·280	·050	·144	·180	—		·590	2 07	·151 ₰	·71	—	·63	—	—	·38
Potash,	—	—	—	·108	—	·029	—	—	·074	—	—	—	—	—	—	—	—	—	—	—
Silica,	22·80	13·500	18·000	15·625	9·960	17·934	7·870	6·975	5·480	11·58	9·900	7·700	17·55	11·60	9 53	18 03	7·23	4·80	15 24	7·02
Carbonic acid,	—	—	—	1 000	14·600	2·512	—	·500	4 500	—	—	2·760	—	·44	6·11	—	—	—	—	—
Phosphoric acid,	2·54	2·155	—	1·235	2·465	·160	trace.	·199	097	·150	·070	·200	·155	—	1·82	—	·07	—	·249	·134
Phosphorus,	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sulphuric acid,	—	—	—	·042	—	·095	trace.	—	trace.	—	—	·500 ‖	·120	—	05	—	trace.	·04	·748	—
Sulphur,	·04	·052	—	—	·050	—	—	·293	—	·030	trace.	—	—	—	—	—	—	—	—	—
Titanic acid,	—	—	—	—	—	—	—	·991	—	—	—	—	—	—	—	—	—	—	—	—
Water,	·80	14 600*	—	12·500	9·650	8·847	17·10	10·050	4·000	9·100	7 050	3 82	15 50	10 25	8·35	—	? Ign. Ore.	—	—	10·71
Organic matter,	—	—	—	0 36†	—	13·36‡	—	—	—	—	—	—	·025**	—	—	5·02	6·49	—	11·10	—
Total	99·96	100 004	94·200	100 063	9 ·279	99·966	99·44	99·512	99·340	100·03	100 000	100·000	99·930	100·24	100·08	100·00	100·10	99·94	100·007	100·144
Total metallic iron	42·94	45 24	43 942	43·50	38·440	56·33	50·70	55·48	54·90	52·83	50·21	53 98	37 89	52·55	42·78	51·30	57 20	65·20	48·25	54·04
Average moisture	—	—	—	1 80	—	13 36	—	5·31	7·77	—	—	—	—	—	—	—	—	—	—	—
Iron in natural ore,	—	—	—	38 36	—	36·33	—	52·55	50·63	—	—	—	—	—	—	—	—	—	—	—

TABLE IV.—CARBONATES.

	Argillaceous Ore from Lias of York-shire, Top of Main Seam, Eston Nab, Cleveland.	Normanby Mines, Cleveland.	Average analysis of Messrs. Chatterley Co.'s Wingbury Mine, Staffordshire.	Average analysis Messrs. Chatterley Co.'s Alley Mine, Staffordshire.	Risley Vein, Weardale.	Brendon Hills, Somerset.	From Coal Measures of Yorkshire, Black Bed Mine, Lowmoor.	From Coal Measures of Derbyshire, Dog Tooth Rake, Staveley.	From Coal Measures S. Staffordshire, Whitestone, Dudley.	From Coal Measures S. Wales, Little Blue Vein, Dowlais.	Carbonate from Portland Limestone Formation, near St. Dizier, France.	Spathose Ore (Calcined), N. Spain.	Spathose Ore from Siegen, Prussia.	Stahlberg, Westphalia, used for Spiegeleisen, Prussia.	Spathose, Eisenerts, Styria, Austria.	Spathic Ore from Indenlerg Iron Co., Austria.	Black Band, Stucker Farm, Tuscarawas Co., N.E. district of Ohio, U. States.	Clay Ironstone, Hanging Rock Region, Ohio, Lawrence Co.	Spathose from Picton County, Nova Scotia	Calcined Black Band.
Ferric oxide,	3·55	2·60	—	—	—	·81	1 45	1·47	·04	·40	·29	77·504	—	—	—	·947	4·61	9·18	—	61·714
Ferrous oxide,	39·01	38 05	58·46	36·20	49 47	43·84	36·14	38·97	48·63	38 77	47·57	2·912	54 779	74 47 *b*	54·91	50·323	50·62 *b*	64·70 *b*	88·59 *b*	7·778
Manganese dioxide,	—	—	—	—	—	—	—	—	—	—	—	1 023	—	—	—	6·998	—	—	—	—
Manganous oxide,	—	·74	·01	1·67	2·42	12·64	1 38	1·09	1·29	1·30	—	—	—	17 08 *b*	1·60 *b*	—	·68	—	2 85	·450 *c*
Alumina,	10·62	5 92	—	4 63	trace.	—	6·74	5·93	3·64	3·28	1 32	3·80	·144	—	—	trace.	4·26	·60	—	4·80 *e*
Lime,	1·70	7 77	2·650	8·68	3 47	·28	2 70	1·62	4·45	4·54	—	·56	1 035	1·34	3·50 *b*	1·848	2·77 *b*	4 60	1·53	—
Magnesia,	3·19	4·16	1·020	1·06	3·15	3·63	2·17	4 82	·80	4·40	—	—	3·261	5·75	3 90 *b*	1·374	2·61 *b*	1·97	·55	8 350
Potash,	—	—	—	—	—	—	·65	·67	·11	·87	—	—	—	—	—	—	—	—	—	2·558
Silica,	10·90	10·36	·080	7 95	4 93	·08	17·37	11·90	6·21	13·55	7·11	7·400	·840	1·08	—	·150	9 32	18 17	2·70	—
Carbonic acid,	25 26	22·00	34·550	31·20	37 71	38·86	26·57	20·14	32·16	30·53	—	—	38·498	—	34·51	38·052	—	—	—	5·900
Phosphoric acid,	2·08	1·07	·400	·80	trace.	—	·24	·48	·31	·46	·10	trace.	·013	—	—	trace.	·40	·11	—	—
Phosphorus,	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1·194
Sulphuric acid,	—	—	1·620 *a*	78 *a*	·08 *a*	—	·11	·05 *a*	·21 *a*	—	·95	—	—	—	—	trace.	·60	—	3·48 *f*	—
Sulphur,	trace.	·14	—	—	—	—	—	—	—	—	—	·65	·029	—	—	—	—	·10	—	1·655
Titanic acid,	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Water,	—	4·45	·130	2·83	—	·18	1·77	1·66	1·55	1·43	35·61 *d*	5·20 *d*	—	—	—	—	—	—	—	—
Organic matter,	—	—	·610	4·10	—	—	2 40	·30	28	29	—	—	—	—	—	—	24·22	—	—	—
Total	96·21	97·27	99 530	100·00	101 23	100·32	99 79	99·10	99·08	99 82	82·95	99·049	85·59	99·72	98·42	99·692	100·09	99·43	99·70	94 399
Total metallic iron	32·53	31·42	—	—	38 56	34 67	29·12	31·24	37·45	30 43	37·20	57·165	24·82	41·70	42·4	29 803	27·97	37·18	42·76	49·70

* + CO_2. † Copper. ‡ Moisture. ₰ CO_2. FeS. ** Oxide Copper.

a Sulphide of iron. *b* Carbonate. *c* Metallic iron. *d* + CO_2. *e* Mn_3O_4. *f* Sulphate of lime.

3. *Brown Iron Ore*, brown hematite, limonite, bog-iron ore, and turgite, are varieties of hydrated ferric oxide. It generally results from the oxidation of the carbonate of iron. It occurs in the more recent formation in beds, but in the primary rocks as veins, often forming the gossan of copper lodes. It occurs largely in Northampton, Lincoln, Gloucestershire, Oxfordshire, Belgium, France, Spain, Portugal, North and South-west Germany, north coast of Africa, Tennessee, and Alabama. In point of purity it is most variable, the deposits in Northampton and Lincoln, evidently changed carbonate of iron, are highly phosphoric, while the enormous deposits of the north and south of Spain and north of Africa are generally free from this deleterious ingredient. Hence these last deposits are now being very extensively opened out to supply smelters with a substitute for Cumberland hematite, hitherto exclusively used for making Bessemer pig. Large deposits of great purity occur in Alabama as true brown hematite. No ore varies so much in its characteristics. It is brown, yellow, or red, seldom massive, and often cindery in appearance. Being generally very porous and a hydrate, it is very easy of reduction; but is often mixed up with large quantities of earthy matter, sometimes sandy, and sometimes full of carbonate of lime. Brown ores are rarely free from phosphorus, except when they result from the peroxidation of spathose ore (see Table III.).

4. *Carbonate of Iron* is very widely diffused. It sometimes occurs comparatively pure, when it is termed spathose, sparry ore, or siderite, and is frequently well crystallized in rhombohedra; but it is generally found massive in veins, which are often of great thickness. This variety is found in Cumberland (Alston Moor), Durham (Weardale), Glamorganshire, Somerset, Devon, Cornwall, Isle of Man, Styria, Carinthia, Westphalia, Anhalt, Pyrenees and Basque provinces, and south of Spain. It is very frequently associated with carbonate of manganese, and when this is present it rapidly loses its pink-white colour, and turns brown, from peroxidation on exposure to moist air. It often happens that the top part of a vein is found to be brown ore, and the lower part spathose; the former being evidently produced by the oxidation of the carbonate. Carbonate of magnesia is sometimes associated with this variety in large quantity. Spathose occurs most frequently in the older rocks, from the carboniferous downwards. Enormous quantities of an impure carbonate occur as a bedded deposit in the lias of Yorkshire. This has given rise to the largest pig-iron producing district in the world, that of Cleveland. The development has taken place at a most rapid rate, and last year (1876) the production of pig iron reached the enormous quantity of over 2,000,000 tons. The ore is of a greenish-grey colour, and coarse sandy nature. Somewhat similar ore occurs in the oolite of Northampton and Oxfordshire; but in these districts it appears to have undergone almost complete peroxidation. It not unfrequently happens that masses are met with in Northamptonshire which appear to have undergone curious metamorphoses. In the centre of a large block of brown ore there will be found a *green* core, having the form of dogtooth spar, and consisting of this impure carbonate of iron. It would thus seem probable that carbonate of lime had first been formed, then a pseudomorph of carbonate of iron, and lastly (by peroxidation), brown iron ore.

Probably the most widely diffused variety of carbonate of iron is that known as clay iron stone, in consequence of its generally occurring in the clay bands of the coal measures. Sometimes it is found in bands, but more frequently in nodules, or "iron stones." The composition of these clay ironstones varies very greatly, but each particular band is tolerably constant. This ore has formed the basis of the iron industry of Great Britain for the last century. One variety is found to be mixed up with a large quantity of carbonaceous matter, and is hence termed "black band," from its glossy black colour. Clay-band ironstone is generally of a dark bluish-gray colour. These varieties occur more or less in most coal formations; but they are particularly important in Scotland, Warwickshire, Staffordshire, South Yorkshire, and South Wales. It also occurs in Shropshire, North Wales, Belgium, Westphalia, France, Maryland, Virginia, Kentucky, Pennsylvania, Ohio, Indiana, Tennessee, and Alabama.

While the ores previously named are generally smelted in their raw state, the varieties of carbonates are usually roasted and converted into higher oxides by a preliminary process. The spathose ores are generally moderately free from phosphorus and sulphur, and yield a very pure iron; the clay ironstones of the coal measures yield a pig iron containing about half of 1 per cent. of phosphorus and sulphur; while the Cleveland stone is very rich in phosphoric acid, and produces a pig with from $1\frac{1}{4}$ to $1\frac{1}{2}$ per cent. phosphorus. These ores after roasting are porous and easy of reduction; but the variation in the gangue which they are mixed up with is very considerable, and requires careful attention from the iron smelter (see Table IV.).

Modes of Extracting Iron from its Ores.—In order to produce metallic iron, it is necessary to subject the ore to heat in a reducing atmosphere. This the ancients and all primitive workers in iron effected by embedding the ore in a mass of fuel, generally charcoal; and in order to facilitate the operation adopted various plans to produce a draught, so as to urge the heat. The most simple plan would evidently be to scoop out a deep hole in the side of a bank, so as to form a chamber for holding the fuel and ore, and so placing the openings at the bottom for the admission of air that the best draught could be obtained. This plan is even now followed in Burmah, no artificial blowing power being used. The furnaces are 10 or 12 feet high, and the air is admitted through clay tubes inserted in the bottom of the chamber. The clay tubes are made by moulding clay around pieces of stick, drying, and burning them. After the furnace has been heated up, charges of charcoal and ore are put in, until the

furnace is full. It is then allowed to burn for about twenty-four hours, and small openings are made at the bottom from time to time to allow the slag to flow away; and when the whole has burnt down an opening is made at the bottom, and the crude lump of malleable iron drawn out. The inhabitants on the west coast of India, the Deccan, and Carnatic go a step further, and make a chamber *purposely* of tempered clay 2 to 4 feet high, generally circular in form, from 10 to 15 inches diameter, with two openings in the bottom, one for the blast, and the other to remove the cinders and lump of iron; while they also supply an artificial blast from a crude bellows made out of the skin of a kid or goat. Two earthen twyers, 12 inches long and 1 inch diameter, are inserted in one side of the furnace, and connected with separate bellows. The furnace is half filled with charcoal, a fire kindled *on* it, and when the fire has burnt *down* sufficiently, the ore and charcoal are charged on top, and the blast kept up till the whole has burnt down, which takes four to six hours. The front of the furnace is then removed, and the lump of iron withdrawn. The inhabitants of Central India and the North-western Provinces make the furnace rather larger, form the iron into a ball in the furnace, by means of an iron bar worked through the top, and then draw the ball out with a pair of tongs. In this way the furnace can be worked continuously, and six lumps of iron, about 20 lbs. each, are obtained in the day of sixteen hours. This variety is in reality the type of the Catalan furnace of the south of France and north of Spain, and was probably the kind of furnace used by the Romans. Similar furnaces are used by the Hottentots of Southern Africa. The Catalan furnaces gradually developed themselves into a four-sided cavity; one side sloping off to afford facility for working the iron, the blast passing through a twyer inserted in the opposite side. The twyer was a conical tube of copper. Bellows were first used to supply the blast; but ultimately water power was applied to generate a blast, by means of the apparatus termed a trompe.

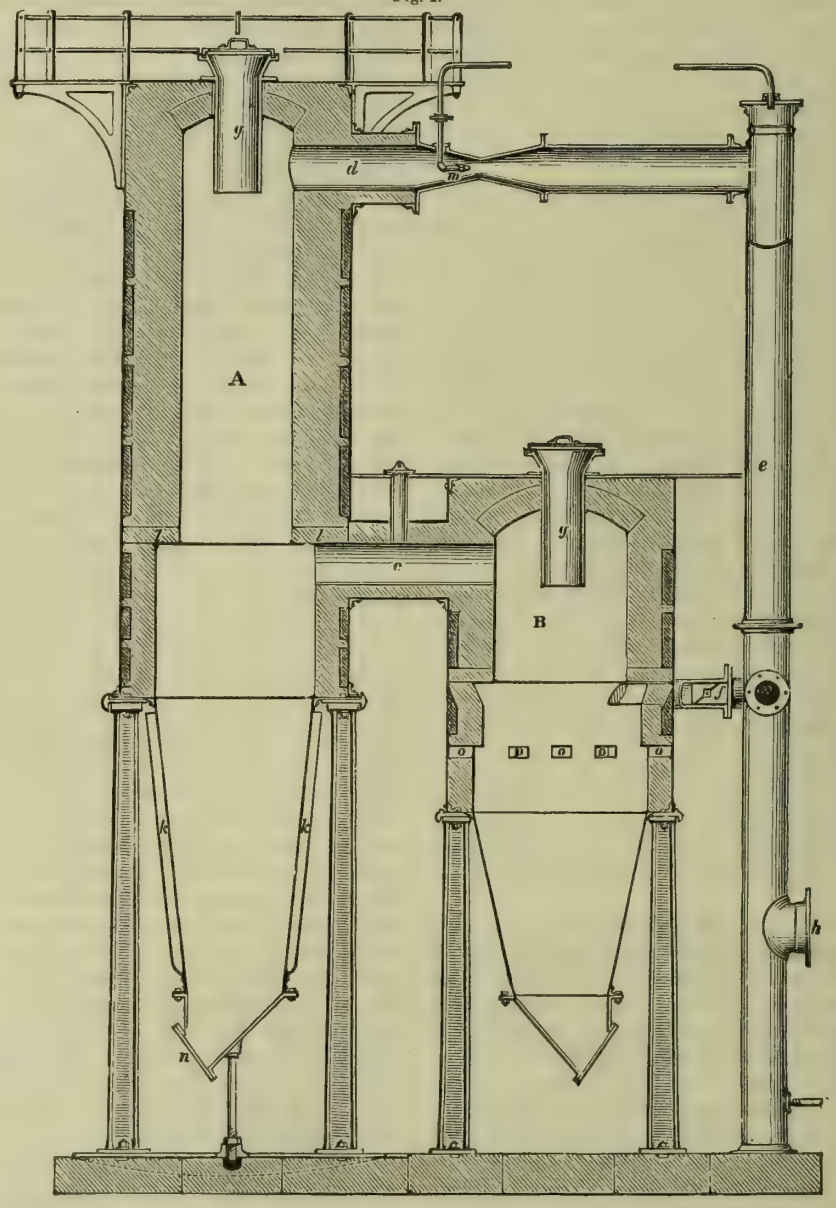
The lump of iron obtained from the Indian furnaces is shaped and worked upon a small flat piece of iron forming an anvil, with hand hammers; but as larger lumps were obtained heavier hammers were required, and strong levers with a heavy mass of iron at one end were used; these being lifted by means of cams on a wheel, which was driven by water-power. The Catalan form of furnace, or "bloomery," as it was termed, gradually increased in height till the German "Stückofen," or "high bloomery" was obtained; and as these got higher, conditions became favourable for the production of cast iron, which was first considered an annoyance to the smelter, but subsequently became his chief product. For a time malleable iron and cast iron were made in the same furnace by modifications of the plan of working; but when cast iron became the chief product, subsequent processes were rendered necessary in order to produce malleable from cast iron. Many attempts have been made to get back to the ancient direct plan of making malleable iron from the ore, but so far none have been thoroughly successful. Clay endeavoured to reduce ore in retorts by heating a mixture of rich hematite ore with one-fifth its weight of charcoal, coke, coal, &c. His patents bear date 1837 and 1840. Quite recently this plan has been revived by Larkin, who thus reduces the finest magnetic ore, then separates the metallic product by a magnet, and melts it up in crucibles with an admixture of spiegeleisen to form steel. The product obtained is of excellent quality, and possibly for such high-priced steel the process may pay; but Clay soon found it would not pay to make common iron in this way. He then attempted to effect the reduction of ore in the puddling furnace, and above 1000 tons of bar iron were made in a small forge at Workington by this process; but the amount of waste, and the cost of fuel and labour combined with the small yield, was so great that it ended in a commercial failure. A somewhat similar process was tried at Cincinnati and Newark by Renton, which also ended in failure. Chenot, at Clichy-la-Garenne, Baracaloo, near Bilbao, and several other places, carried out the direct formation of metallic iron from the ore on a large scale for some years, from 1846 to 1855. His reducing furnace consisted essentially of a number of vertical rectangular chambers, or retorts, heated by *outside* flues, and widening towards the bottom to facilitate the descent of the charge. Two methods of effecting reduction were tried; first, the ore was mixed with carbonaceous material to deprive it of its oxygen: secondly, the reduction was effected by a current of hot carbonic oxide, this gas being generated in a separate producer by blowing air through charcoal. The reduced material was dropped into a close waggon by a special arrangement for preventing access of air. The metallic sponge thus obtained was balled in a charcoal hearth, and a very fine soft iron was thus obtained, but at a great cost.

Various other attempts have been made in the same direction, and many feasible plans have been suggested, but not tried. Among these latter may rank the plan patented by Henderson of Glasgow, and afterwards, but quite independently, by G. J. Snelus, which consisted in reducing the ore to a fine powder, and after drying and mixing with reducing material, allowing it to fall through the form of furnace known as the "Gherstenofer," the chamber being either heated externally, or else by heated carbonic oxide gas. The Gherstenofer furnace is a vertical brick chamber, containing a number of horizontal angular bearers in series one above the other, so arranged that the ore fed in at the top is intercepted in its course, and drops from bearer to bearer to the bottom. The original furnace has been used very successfully for calcining copper pyrites, and it was thought that by keeping the chamber filled with a reducing atmosphere in place of an oxidising one metallic iron would readily be formed. Experiments made some years ago proved that under favourable conditions, *i.e.*, with very finely divided material, and in a good reducing atmosphere, oxide of iron could be reduced in a minute or two, and at comparatively

low temperatures. The process suggested would be a continuous one, cheaply worked, and capable of dealing with considerable quantities of material in a short time. It may yet be worked out to a success. The reduced iron would be in the form of a fine powder, and would require to be compressed, and then melted up in a Siemens or other furnace.

The most recent attempts at producing iron direct from the ore have been made by Blair of Pittsburg. Ireland is now attempting to introduce his plan into this country. The following is a description of this modification of Chenot's ideas:—A is the chamber, in which the ore is placed in medium sized lumps, being charged through the hopper, *g*; B is

Fig. 1.



the gas producer, charged with coal through the hopper, *g*; *o*, *o*, *o*, are openings for admission of air, which is drawn in by the action of the steam jet, *m*; *k k* is a water casing to assist in cooling the reduced ore before drawing it at the door, *n*; *e* is the gas main, and *f* a valve for allowing a portion of the gas to pass into the producer, so as to prevent it working too fast.

A very curious mode of reducing iron ore, and at the same time refining pig iron, was tried in this country some eight years ago by Blair, who had been working it previously in the United States. It was called the Ellershausen process from its inventor, and consisted in mixing molten pig iron in layers (sandwich fashion) with iron ore, and then subjecting the sandwich to heat. This caused the ore, carbon.

and silicon in the pig to react upon each other, and while the carbon and silicon were oxidised the ore was reduced, and the mass thus became malleable iron. The product obtained, however, was very irregular, the operation wasteful, and it was soon abandoned.

This process is to some extent similar in principle to the Uchatius process of steel making, which created considerable stir at the Paris Exhibition in 1855. By this plan granulated pig iron and iron ore were melted together in certain proportions, in crucibles. The carbon and silicon in the iron were burnt out by the oxygen of the ore, and steel, more or less hard, was the result. The process failed in most places, because the effects of phosphorus and sulphur were not then well known. It was, however, carried on for some years at Wykmanshyttan, in Sweden, where very pure pig iron and magnetic ore were used. The manufacture is costly when the melting is conducted in pots; but the Landore Steel Company have made the plan a practical success, by melting the pig iron and ore upon the open hearth of the regenerative furnace. The further consideration of this plan must be reserved for the article on Steel, as it can scarcely be deemed a direct method of obtaining iron. Dr. Siemens has, however, invented another plan of getting at this much to be desired object. He has been working at the subject for some years past, and the plans are now fairly perfected. The furnace (see Plates II. and III. of article Fuel) consists of a wrought-iron drum, 10 feet long by 8 feet 6 inches in diameter inside, is mounted on four antifriction rollers, and by means of a small engine can be rotated quickly or slowly as desired. The drum is lined inside with $2\frac{1}{2}$ inches ordinary firebrick, and the ends with bauxite bricks. Roll scale is melted on the bricks and allowed to set in flats round the drum, until a lining from 4 to 6 inches thick is formed.

The source of heat is the usual Siemens' producers, with two gas and two air regenerators. The extremities of the cylindrical rotative chamber are closed, with the exception of the central portion, 4 feet in diameter; the one on the side of the regenerators serves for the introduction of the heated gas and air, as well as for the exit of the products of combustion, and the other facing the working platform is closed by a door hung in the usual manner. The passage for the introduction of gas and air from the regenerators is separated by a vertical diametrical wall, 15 inches thick, from the passage through which the products of combustion pass away, the gas and air being reversed in the ordinary way. A tap-hole is provided at the front of the furnace, on a level with the lining, for discharging the slag into a cave below, where it is received into common slag bogies.

The charge, consisting of a mixture of ores, limestone, and coal, is broken up, by means of a crushing mill, into small fragments about the size of peas, and well mixed together. This is then thrown into the furnace by means of scoops. As soon as the charge is in, the damper is shut down, the gas and air are completely shut off, and the furnace slowly rotated until the hydrocarbons are nearly burnt off; then the gas and air are gradually turned on and the mass is thoroughly heated. The coal combines with the oxygen of the ore, which is formed into a lower oxide ($Fe_2O_3 + C = 2FeO + CO$), and this again becomes reduced to metallic iron when it comes in contact with more coal ($FeO + C = Fe + CO$), whilst the silica of the ore combines with ferrous oxide and lime to form a fusible slag. During this last reaction a minimum amount of gas and a maximum quantity of heated air are admitted into the furnace. A great economy of heat is thus effected, as the carbonic oxide which is being evolved combines with the oxygen of the air and gives out an intense heat, forming carbonic acid. When this reaction is nearly completed the amount of gas entering the furnace is gradually increased, and only enough air is admitted to form a complete combustion with the gas. A great heat is thus obtained, and the slag becomes perfectly liquefied; the rotator is then stopped in a suitable position, and the slag is tapped off. The rotator is again set in motion, and the particles of spongy metallic iron, on coming in contact with one another, adhere together and form into six or eight balls, which are grasped by means of large tongs and lifted out of the front orifice, carried to a steam hammer, and shingled in the usual way of consolidating puddled balls.

A few rough lumps of any very refractory ore are then thrown in the bath of cinder which has formed at the bottom of the furnace, and these are allowed to set so as to make the lining as rugged as possible, the charge being thus turned over more effectually than by a smooth surface. So the furnace really is self-fettling, and the lining can be kept any thickness without much trouble. As soon as the lumps and cinder have set, the furnace is ready for another charge. The time occupied by a charge is about three hours, and six or seven charges can conveniently be made in twenty-four hours. The loss of iron has been found to be about 20 per cent., and the iron produced is almost chemically pure, though the ores and fuel may contain large amounts of phosphorus and sulphur.

Up to the present time the blast furnace has afforded the only means of reducing iron upon the large scale economically. Essentially the blast furnace consists of a vertical chamber, somewhat like a barrel on end, but very tall in proportion to its diameter. The ore, fuel, and a flux are charged into the top, and air is blown in through apertures near the bottom. A hole at the bottom serves for drawing off the molten iron, and one a little higher up for the slag. Great modifications have taken place in the size and shape of blast furnaces during the present century, the object being to increase the production per furnace, and to reduce the quantity of fuel required for the process (see Plate II.). The discovery of the effect of heating the blast was made by Neilson, and the economy in fuel thereby produced has led to a constant increase in its temperature, until it is now often used red-hot. The

heating of the blast requires a separate apparatus, which is termed a stove. The hot-blast stoves have also undergone great modifications, until now they take up more room and are about as costly as the furnace itself.

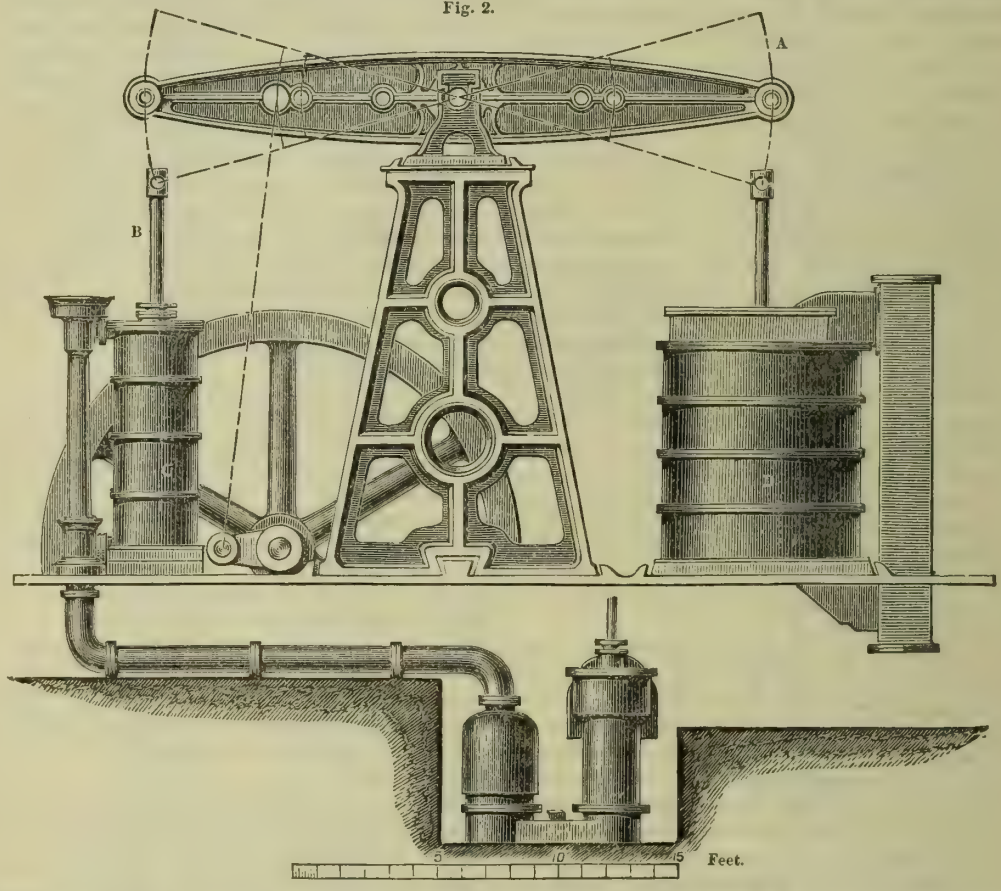
The blast engines of the present day are very perfect contrivances, and frequently run from year's end to year's end without stopping. Three distinct types are recognized:—

1. The *beam engine*, which is illustrated by Figs. 2 and 3, and Plate I. It will be seen from this that a heavy reciprocating beam, *a*, moved by the piston rod, *b*, of steam cylinder, *c*, on one side, moves the piston of a larger cylinder, *d*, on the other side, in which the blast is raised to the required pressure.

2. The grasshopper engine. In this type the beam is supported at one end by a vibrating arm, and at the other end it is joined to the piston rods of the steam and blast cylinders, the two cylinders being in line with the beam.

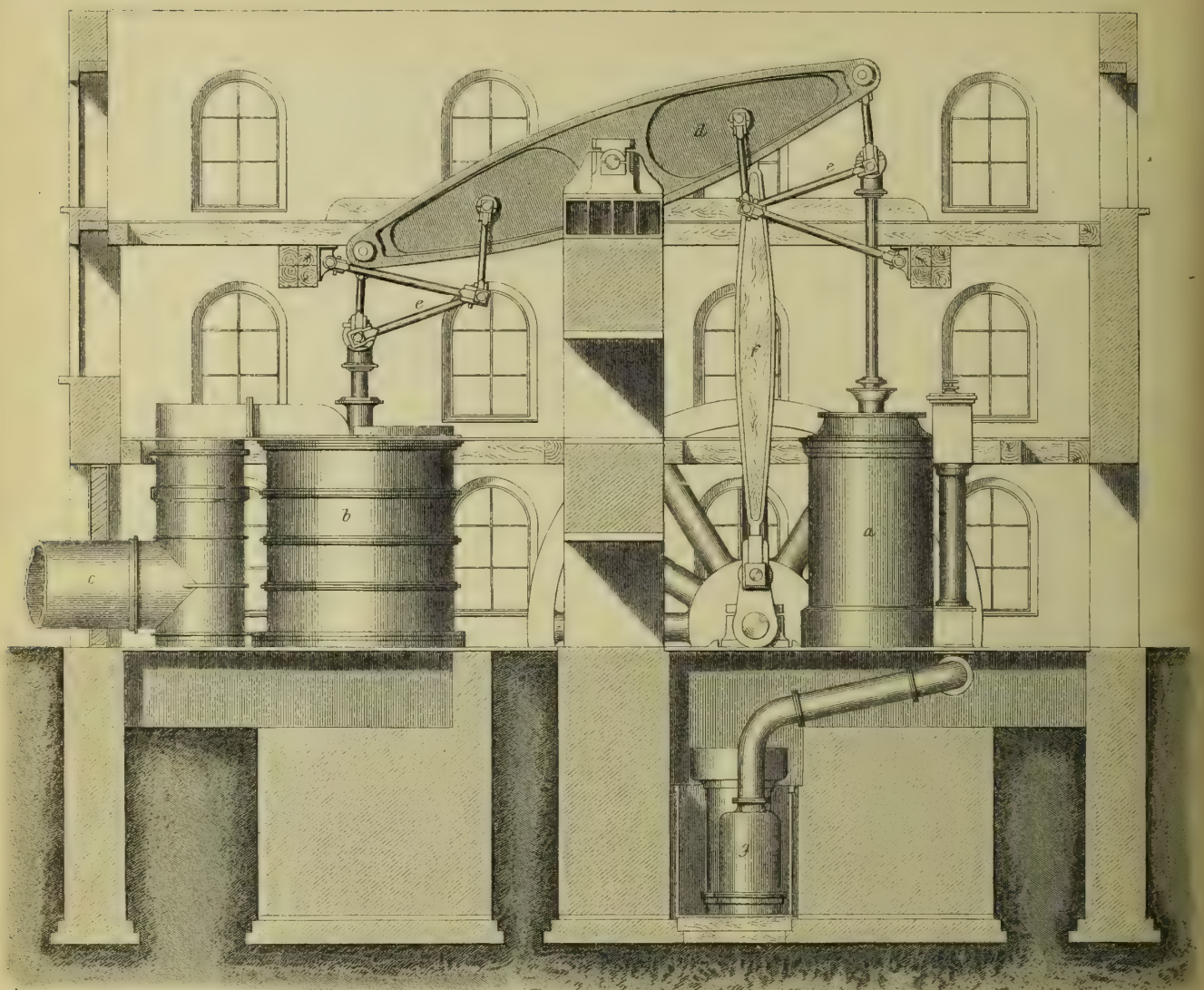
3. The vertical engine. This type is largely used in the Middlesborough district. The beam is dispensed with, the two cylinders are placed vertically one above the other, and the piston rods are made continuous. This engine can be run at higher speeds than the beam engine, but it has the defect of a short stroke. In a modified form of this type the cylinders are placed side by side, and the piston rods joined to a cross head.

Fig. 2.



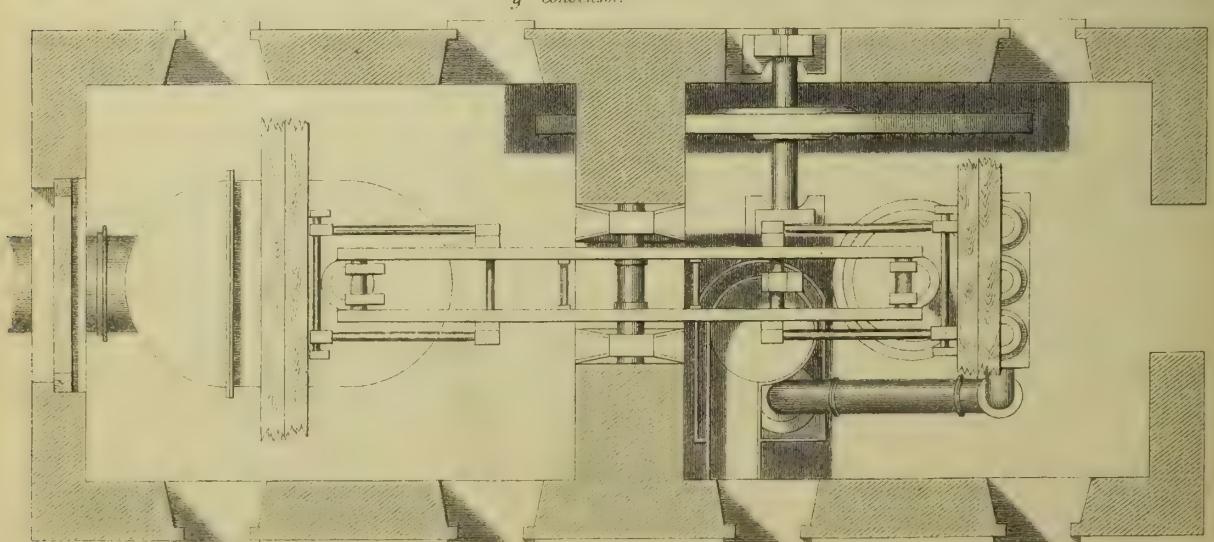
The following description (Fig. 2, Plate II.) will serve to explain the principal parts of a blast furnace :—*h* is the crucible or well of the furnace. The bottom of this is termed the hearth. The furnace gradually widens out above the crucible, forming an inverted cone, the sides of which, *g*, are termed the boshes. There has been very great variation in the steepness of these sides, or "angle of the bosh." Formerly they were very flat, making an angle of about 45° with the horizontal; but the modern tendency is to make them much steeper—up to an angle of 75° or 80°. The top of the boshes is the widest point in the furnace, and the term "diameter of the bosh" is understood to mean diameter at this point. From the top of the bosh the furnace gradually narrows into the mouth, *b*. The mouth of the furnace is now usually closed by a cup and cone of iron, the cone being suspended below the cup, so that by lowering the former an annular space is left for the materials to pass into the furnace. When the cone is drawn up, it closes the aperture in the cup completely, and an opening is therefore left in the side of the furnace below the cup for the escape of the gases going off from the furnace. As these gases contain a large portion that is combustible, they are led off

BLOWING ENGINE, EBBW VALE, SOUTH WALES.



REFERENCE.

a. Steam cylinder. *c.* Blast main. *e.* Parallel motion.
b. Blowing cylinder. *d.* Engine beam. *f.* Connecting rod.
g. Condensor.



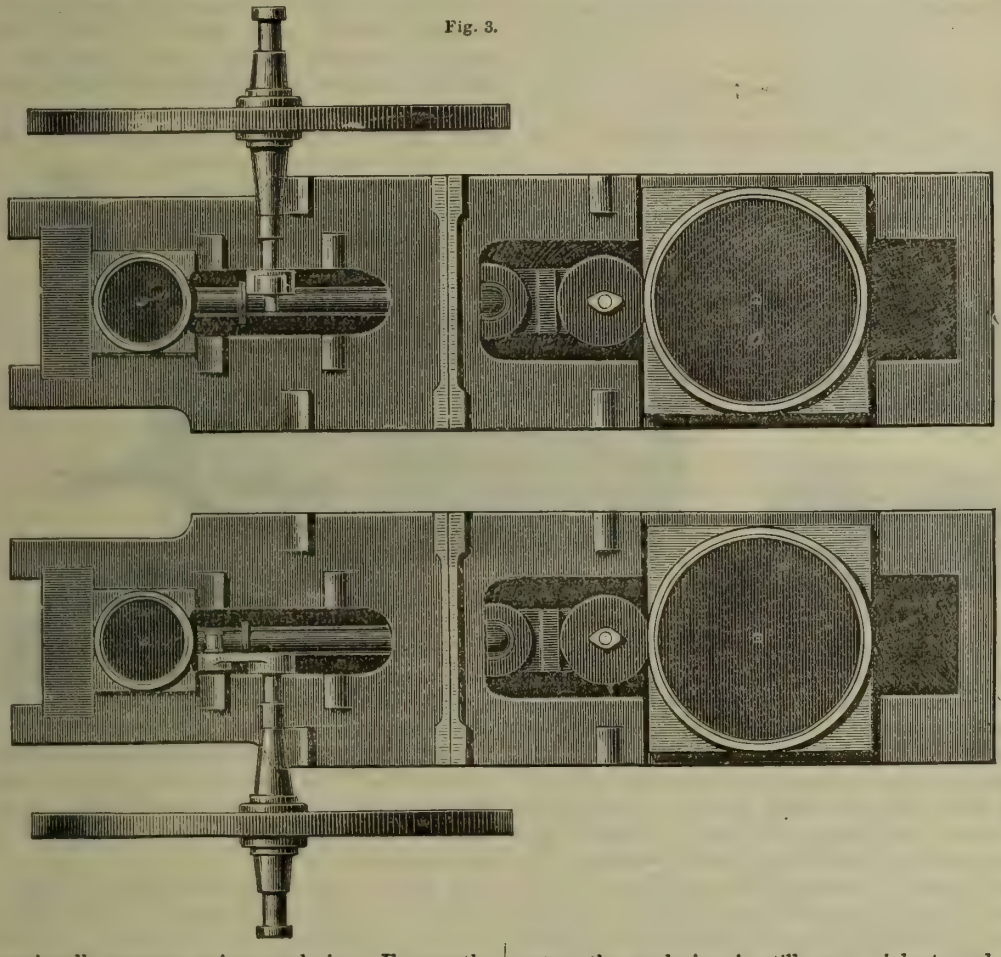
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Ins 12 0 5 10 15 20 25 30 Feet

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through the "gas box," *c*, and "down-comer," *d*, to be burnt either in the stoves or under the boilers. The openings, *l l*, in the top of the crucible are termed the twyer rooms. The pipes which convey the blast into the furnace are termed the blast mains. A circular main, *m*, surrounds, or partly surrounds, the furnace, and is termed the horse-shoe main. From this branches descend to distribute the blast around the furnace. The ends of these branches are formed in separate pieces. The portions projecting into the furnace are termed the twyers, and the next piece which fits into these, *j*, is termed the swan neck or belly pipe. When hot blast is used, the twyers have to be kept cool by water. There are several methods of doing this. The coil twyer (Figs. 4, 5) consists simply of a wrought-iron tube twisted into a cone-shaped spiral, the water being forced in at one end and issuing at the other. The spiral is luted on the inside with clay, and the wrought-iron nose of the twyer is forced into it. Sometimes cast iron is run around the spiral, thus forming a solid twyer, with a water-course through it. The water circulating through these twyers is supplied at a considerable pressure; and when the nose of the twyer gets burnt off (an accident that very often occurs), the water forces itself into the furnace, and

Fig. 3.



occasionally causes a serious explosion. Frequently, however, the escape of water into the furnace does no more than derange the working of the furnace. The exact cause of the violent explosions which sometimes occur is rather obscure; but it is probably owing to a considerable volume of water entering the furnace, and a slip of the material above taking place at the same time, some molten iron falls into the water, and either decomposes it into oxygen and hydrogen, which afterwards reunite, or else produces instantaneously a large volume of steam. The sharp nature of the report favours the first view; and it is well known that when molten steel falls into water, the explosion is still more violent, and no large volume of steam appears to be disengaged. When water is run *on* to molten iron or steel, no violent explosion takes place, although plenty of steam is generated.

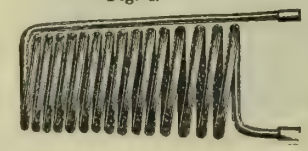
As it is most important not only to prevent explosions, but also to guard against the derangement of the furnace, it is obviously advisable to use twyers that are not subject to this defect. Lloyd's patent spray twyer (Fig. 6) fortunately overcomes the difficulty.

There is considerable difference of opinion as to the best number of twyers for a furnace. In prac-

tice they generally vary from three to eight. Five is by far the most usual number. It is important to distribute the blast evenly and sufficiently, but at the same time, it is necessary to keep a sufficient volume passing through each twyer, that it may force its way into the centre of the furnace and not creep up the sides. For the same reason, it is often found advisable to push the nose of the twyer well into the furnace, sometimes as much as 12 inches from the brickwork. The size of the twyeres must be regulated to the volume of the blast which they are to carry into the furnace. Like everything else, the tendency has been to increase their size. Formerly they were from 2½ to 3 inches diameter; now 5 inches is no uncommon size, and the Solway Company, when making the very large quantity of over 800 tons of Bessemer iron per week from one furnace, used one 5½-inch and five 6½-inch twyers, while at the Lucy Furnace, Pittsburg, 8-inch twyers are used.

In addition to the openings into the bottom of the furnace for twyers, there are two others, one at the bottom of the crucible for the exit of the molten iron, the other higher up, for running off the slag. In the older forms of furnaces it was customary to leave a considerable opening in the front part of the crucible, and to make a chamber on the outside, which was termed the fore-hearth. An arch was turned over the opening, termed the tymp arch, and a water-cooled rectangular casting was placed under the arch, sometimes horizontally, and sometimes with its flat face vertical. This was termed the tymp plate. The front part of the fore-hearth was protected by a similar water-cooled plate, termed the dam plate. This had a notch at its top edge, termed the cinder notch, and over this the cinder was allowed to flow. A hole in the bottom of the dam plate formed the tap hole for the metal. This hole was, however, frequently put on one side of the dam plate, so that it could be the more easily raised if the furnace was working badly, and the material setting on the bottom of the hearth. The fore-hearth was usually partially filled up with ashes after each tapping, which lifted as the molten slag and iron accumulated,

Fig. 4.



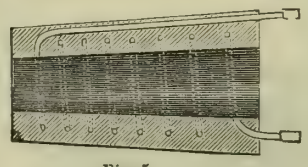
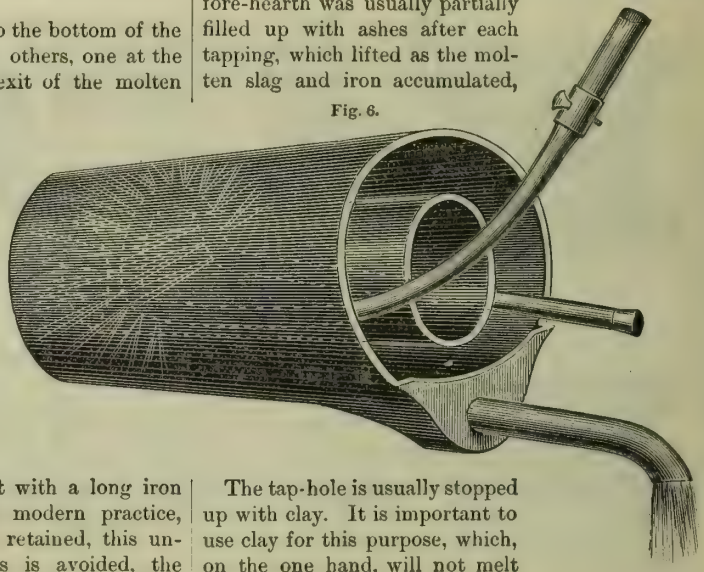


Fig. 5.

Fig. 6.

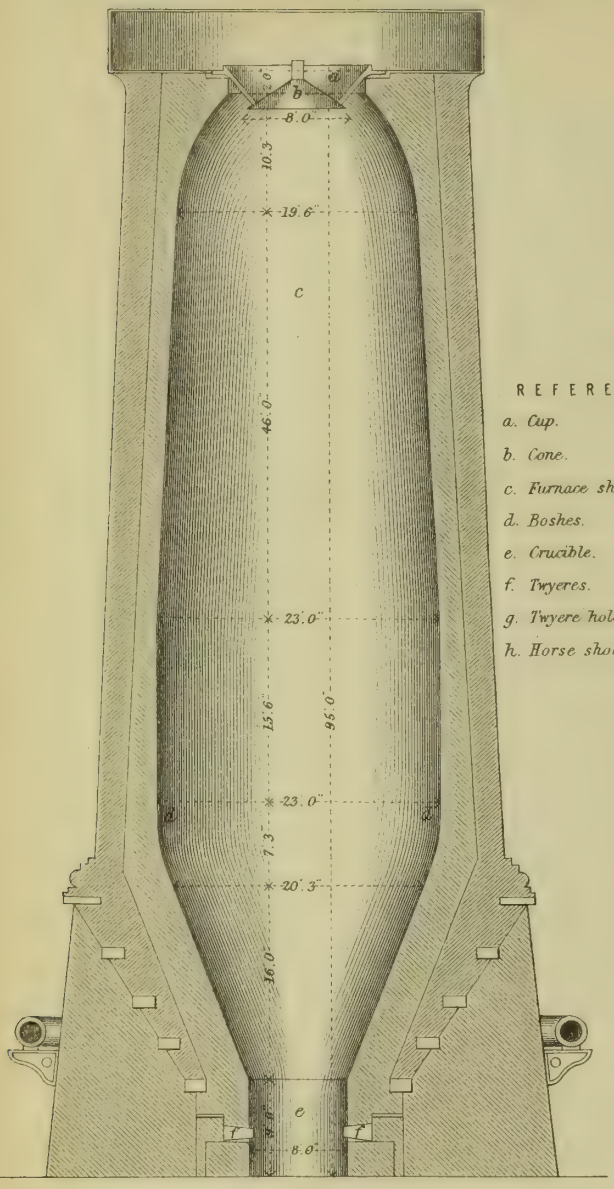


and were laboriously scraped out with a long iron scraper after each tapping. In modern practice, even where the fore-hearth is retained, this unnecessary and wasteful process is avoided, the fore-hearth being covered with a covering of clay, which is weighted down, and the slag is allowed to flow through a small hole made by pushing an iron bar through the clay. Lührman does away with the fore-hearth altogether, and provides two separate openings in the crucible, one for the exit of the slag at a point about 15 inches below the twyers, and the other at the bottom of the crucible for the metal. The slag hole is protected with a water-cooled block, having a perforation in it about 6 inches in diameter, and into this is placed a smaller water-cooled block of brass, having a hole in it just large enough to allow the slag to run through as fast as made. This is a very neat arrangement, and answers well. Occasionally, when the slag gets very thick from containing too much lime or alumina, it will not flow through the small hole, and the little block itself has to be removed and the slag allowed to run out of a temporary hole made in the clay-stopping put in its place. With ordinary care, however, this does not often occur.

The tap-hole is usually stopped up with clay. It is important to use clay for this purpose, which, on the one hand, will not melt too easily, and on the other does not bake too hard. A mixture of 2 parts fire clay and 1 of small coal ground together forms a very useful black stopping clay, which rarely if ever leads to "hard taps," as they are termed.

In order to get at the twyers easily, the superstructure of the furnace is supported either by four or five brick pillars or by iron columns. A strong circular iron casting (generally made in segments) is placed on the top of the pillars or columns, and the upper part of the furnace rests upon this. The furnace itself is built of the best fire brick, and the upper part is either altogether cased with three-eighths wrought-iron casing, or is braced together by a series of iron hoops. It is highly important that the bricks used for the lining, at least, of the furnace, should be free from oxide of iron, as it has been shown by Pattinson and Wood that carbonic oxide will reduce the oxide of iron, and that the process of carbon deposition discovered by I. L. Bell may go on to such an extent, as

BLAST FURNACE, ESTON IRON WORKS.

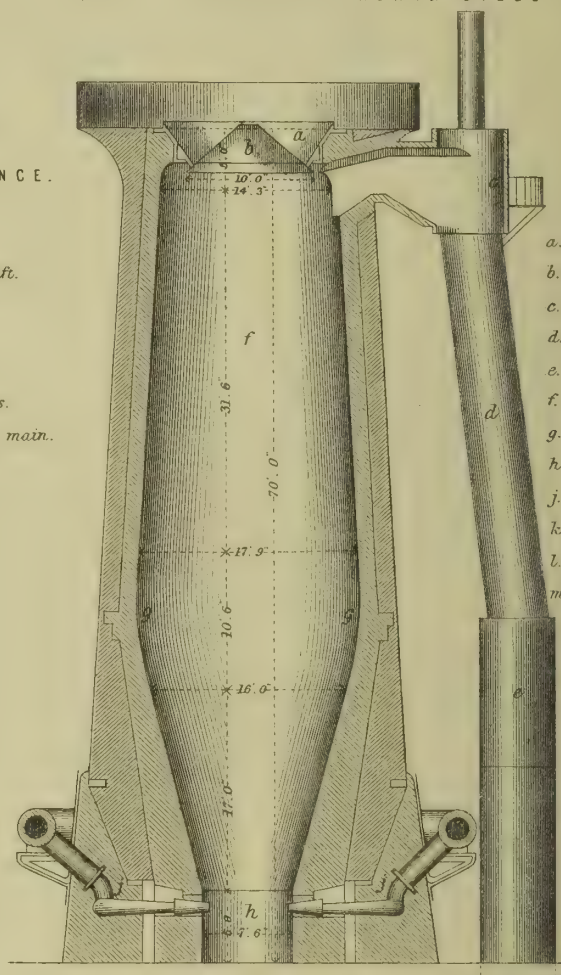


REFERENCE.

a. Cup.
b. Cone.
c. Furnace shaft.
d. Boshes.
e. Crucible.
f. Twyeres.
g. Twyere holes.
h. Horse shoe main.

Cubic Contents 28800 Feet.

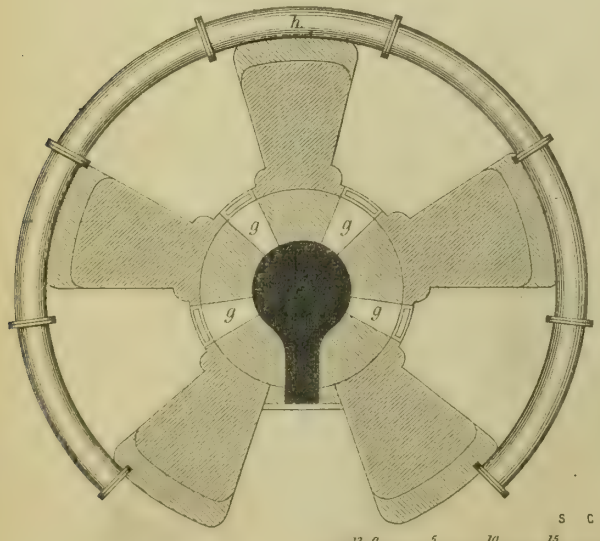
BLAST FURNACE,
WEST CUMBERLAND IRON & STEEL WORKS.

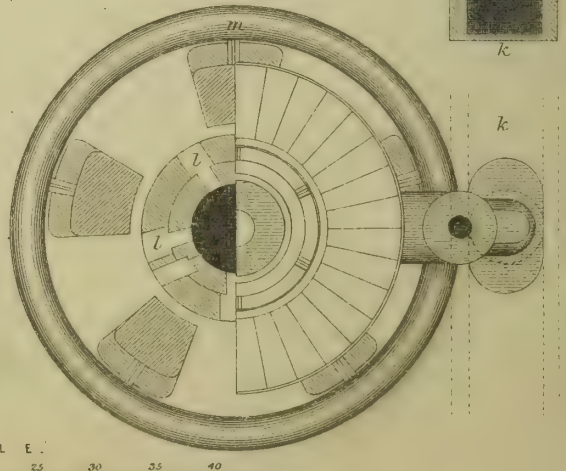


REFERENCE.

a. Cup.
b. Cone.
c. Gas box.
d. Gas downcomer.
e. Dust box.
f. Furnace shaft.
g. Boshes.
h. Crucible.
j. Twyere pipes.
k. Gas culvert.
l. Twyere holes.
m. Circular main.

Cubic Contents 10388 Feet.





SCALE.

12.0 5 10 15 20 25 30 35 40
Ins. Feet

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to entirely disintegrate the bricks and thus destroy the furnace.

The top part of the furnace is covered in, and so

Fig. 7.

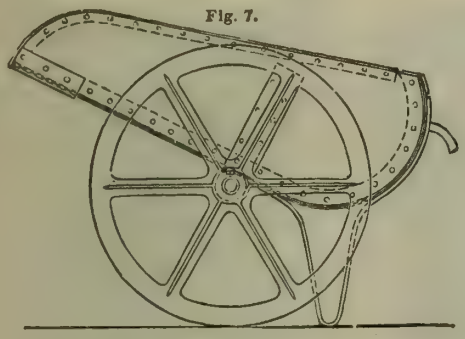
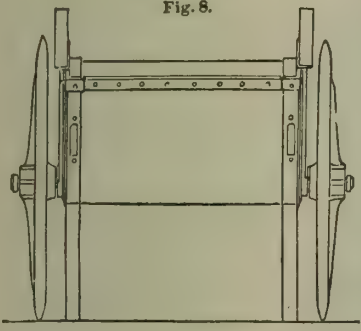


Fig. 8.



expanded as to form a gantry, giving sufficient room around the charging hole for the charging barrows to be wheeled conveniently. The charging hole is generally protected by a cylindrical structure of sheet iron (sometimes lined with brickwork), termed the tunnel head. Openings in this admit the charging barrows to be tipped. In England these charging barrows are usually made so as to hold about $5\frac{1}{2}$ cwts. coke and 8 to 10 cwts. of ore and limestone, and sufficiently handy for one man to wheel. Figs. 7 and 8 will explain themselves.

At Creuzot, in France, much larger charges are used, and the trucks are run right over the charging cones, and the bottoms dropped.

Hot Blast.—Since Neilson's discovery of the use of the hot blast numerous modifications have taken place in the apparatus used for heating the blast. The apparatus is usually termed a "hot-blast stove," and two forms are now well recognized. The oldest is the cast-iron stove, in which the blast is heated by passing it through a series of iron pipes, which are kept at a dull red temperature by either a coal fire or by burning the waste gases of the blast furnace. The more modern or fire-brick stove was an adaptation by Cowper of Siemens' regenerative principle. This was further improved by Whitwell. The plan consists in using two or more air-tight chambers lined with fire brick, and with an arrangement of loose brickwork in the interior, so disposed that the gases which are burnt at one point give up most of their heat to the brickwork before they leave the chamber. When the brickwork has been sufficiently heated the gas is stopped off, and the blast admitted in such a way that before leaving the stove it has passed over the hot brickwork and become raised to the required temperature. While one stove is being

Fig. 9.

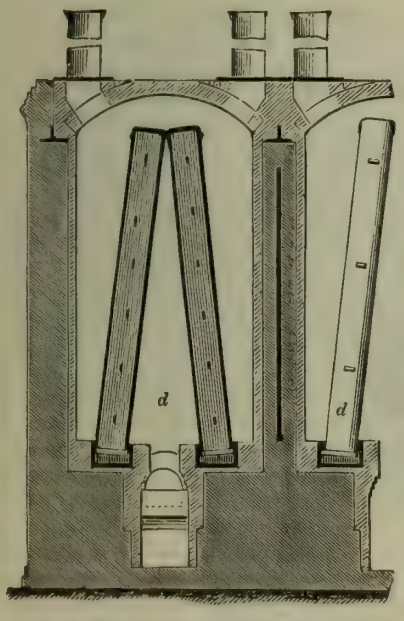
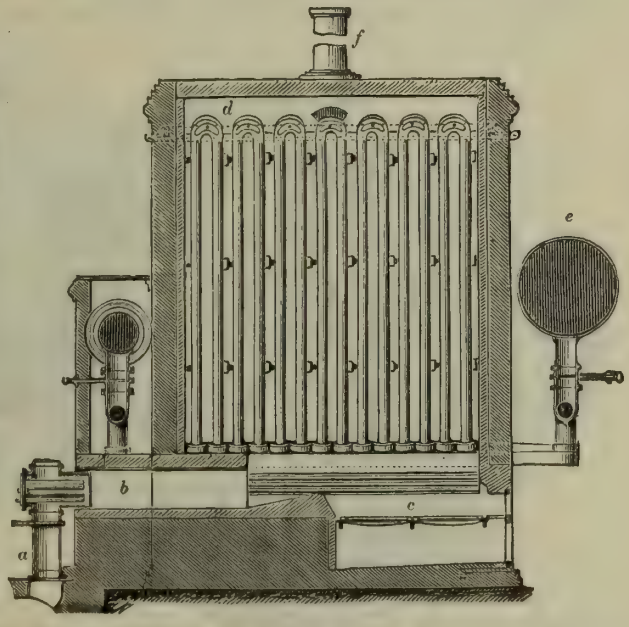


Fig. 10.



cooled down by heating the blast the other stove is being heated up to be in turn cooled down. The temperature to which the blast can be raised in cast-iron stoves is limited, because the cast-iron pipes soon become destroyed if the heat is too great. A constant temperature of about 1000° Fahr., or sufficient to

keep zinc melted, is a very good result from cast-iron stoves; but with fire-brick stoves it is easy to get 1500° to 1600° of heat. The accompanying sketches will sufficiently explain the leading principles of the two classes of stoves. Figs. 9 and 10 are those designed by J. Gjers, which are much used at the present time. *a* is the gas inlet; *b*, combustion chamber; *c*, fire-place for use when coal is burned; *d*, cast-iron pipes through which the blast is passed; *e*, cold blast main; *f*, hot blast main. Fire-brick stoves were first patented by Cowper, but those of Whitwell, which are more easily cleaned, are most in favour. Figs. 11, 12, 13, and 14 represent Whitwell's stoves. Fig. 11 is a section through A—B, Fig. 12; Fig. 12 a section through E—F, Fig. 11; Fig. 13 a section through C—D, Fig. 12; Fig. 14 is a plan. A is the hot blast outlet; B, gas inlet; C, combustion chamber; D, air holes; and E, cold blast inlet and gas outlet.

Fig. 11.

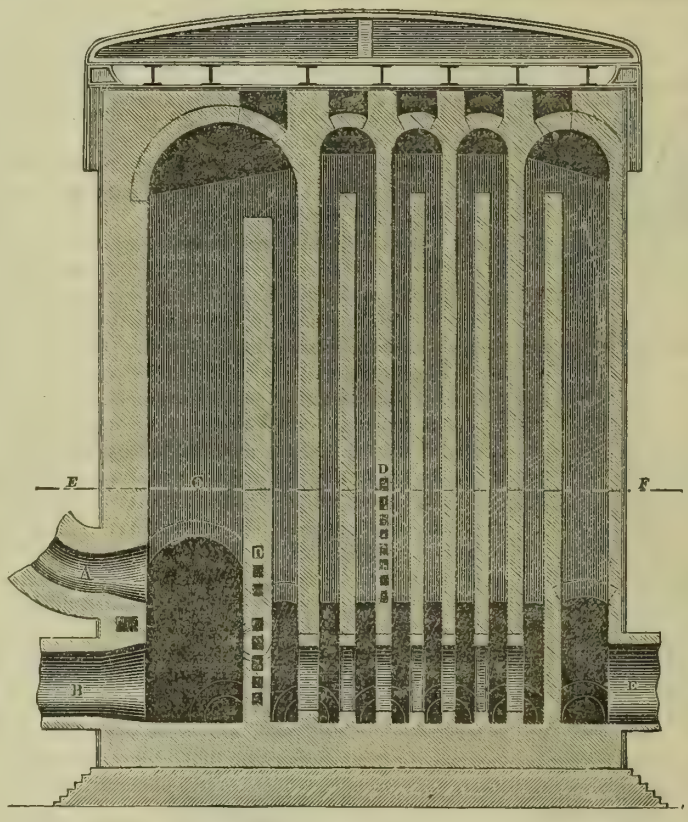
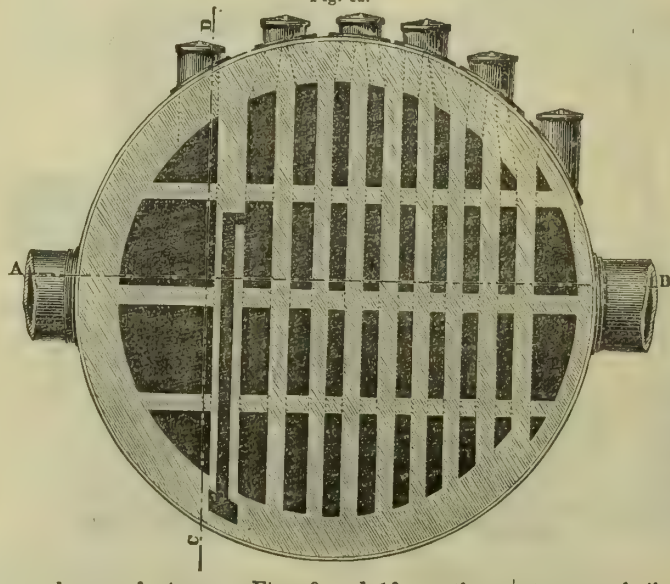


Fig. 12.

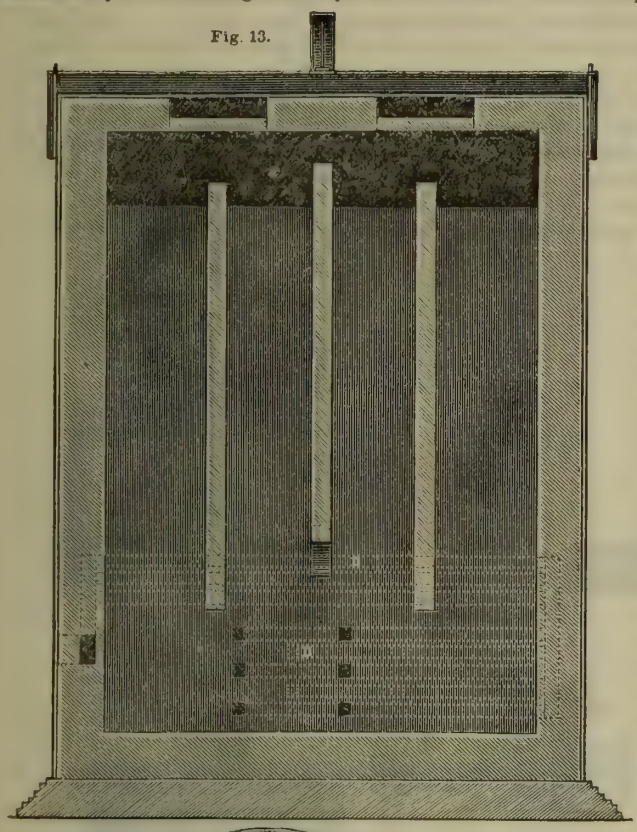


Method of Collecting the Gas from Blast Furnaces.—Various plans of taking off the gas from the tops of furnaces have been devised; but these have now nearly all given place to the cup and cone arrangement. By this plan the top of the furnace is closed in, and into the mouth is fitted a cast-iron frustum of a cone, point downwards. Another cone, point uppermost, is suspended in the opening of the cup; and having its base slightly larger than the opening in the cup, it is capable of closing that opening altogether when drawn up. The materials forming the charge are tipped into the cup, and when the cone is lowered they fall into the furnace through the annular space between the cup and the cone. They thus distribute themselves regularly around the furnace, and the larger lumps naturally roll into the centre. This is a point of extreme importance, because by so doing the centre of the furnace is kept open for the ascending gases, which conduces greatly to the regular working of the furnace. If the lumps are all allowed to fall on one side, the gases will work up that side and the material will come down most irregularly, producing variable and low grades of iron. The furnace being closed against the escape of gas at the top by the cone, an opening is left in the side, and an iron box, termed the "gas box," is fixed at this point. A large wrought-iron tube, termed the "down-comer," is joined to the gas box, and the gases pass off through the side opening in the furnace, gas box, and down-comer to the "gas main" or "culvert," to be utilized at the stoves or boilers.

The iron cup is suspended at one end of a balanced

iron beam, the other end of which is coupled to a winch or hydraulic arrangement by which it is lifted into its place when the charge has dropped into the furnace.

Fig. 13.



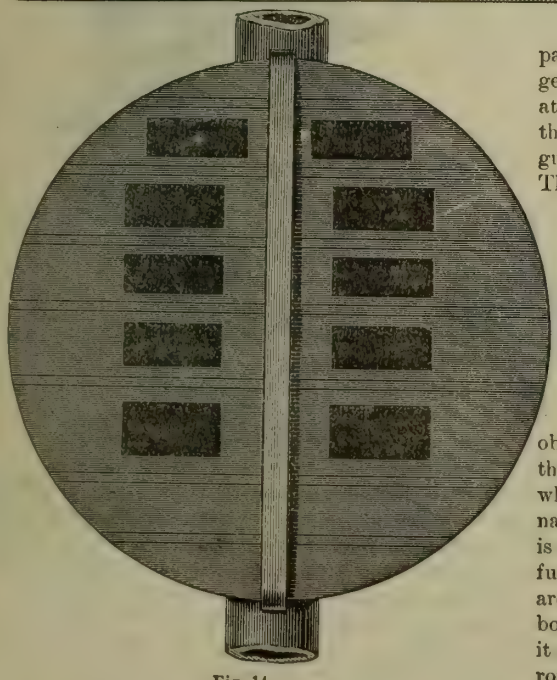


Fig. 14.

Drying and Blowing in.—After a furnace has been built it requires very careful drying. This is usually done by building a fireplace in the crucible (taking care to protect the crucible bricks from the fiercest heat), and keeping a moderate fire burning continuously for two or three months. When quite dry a quantity of timber is placed in the crucible, and then a few tons of coke, after which a light charge (that is, one in which the coke preponderates over the ore) is added, till the furnace is nearly full. The timber is then lighted and allowed to burn up very slowly, the bell being kept carefully open all the time, until the steam has disappeared and the gas "fires" at the top of the furnace. The blast may then be put on, and when the gas at the top is burning well the bell may be closed.

Method of Raising Material to the Tops of Furnaces.—At some old works, such as Dowlais, the furnaces are built against a steep bank, so that the materials can be wheeled from depôts on the bank direct to the furnace tops; but at most works some plan for hoisting the material is necessary. The most simple, and probably the cheapest in working, is a small pair of reversing engines, so arranged as to give motion to a small driving pinion which is coupled to a large tooth wheel placed upon the same shaft with a couple of drums. A wire rope is fastened to each drum, and thence passes over a large pulley placed upon head gear at the top of the furnace, and is securely attached at the other end to the cage for lifting the barrows. The cages carry "shoes," which work on guides from the bottom to the top of the furnace. The ropes are so arranged that while one cage is going up the other is coming down, and they thus balance each other. The framework of the "hoist" is sometimes formed by four or more iron columns braced together, and these carry the guide. Three stiff columns form a very simple and efficient hoist for a couple of cages, if well put together. Sometimes the hoist is walled in, forming a tall shaft in which the cages work. Where a natural head of water can be obtained a water balance hoist is very economical. In this case the two cages are connected by a wire rope which passes over a large pulley at the top of the furnace. Under the barrow platform of each cage there is a water box that can be filled at the top of the furnace, and empties itself at the bottom. Matters are so arranged that when water is run into the box under the empty cage at the top of the furnace, it overbalances the other cage with its loaded barrows and empty box, and therefore lifts it to the top of the furnace. Severe frost is the chief drawback to this simple and cheap arrangement. Pneumatic and direct steam hoists are also employed at various

works, but are less common than the above. Figs. 15 and 16 is Gjer's pneumatic hoist—*a*, air pump; *b*, tube; *c*, piston; *d*, barrow cage. At Creuzot a direct hydraulic lift is used, and answers well for moderate heights; and at the Clarence Works all the furnaces are fed by a neat hydraulic arrangement constructed by Sir W. Armstrong, in which the stroke of the ram is multiplied by passing the rope around a five sheave pulley attached to the head of the ram.

Slagging Arrangements.—The earthy matter of the ore and fuel unites with the flux to form a slag, which is either run off from the furnace down the "fall" continuously, or is tapped off at intervals. As the quantity of the slag is very considerable, varying from 10 to 30 cwts. per ton of iron, organized means for removing it are necessary. It is usually run into iron boxes placed loosely upon bogies, and when the boxes are full the bogies are drawn on one side to cool. As soon as the slag has set the loose box sides which taper upwards are drawn off, and the ball of slag is tipped over the slag heap.

It is very convenient to have matters so arranged

Fig. 15.

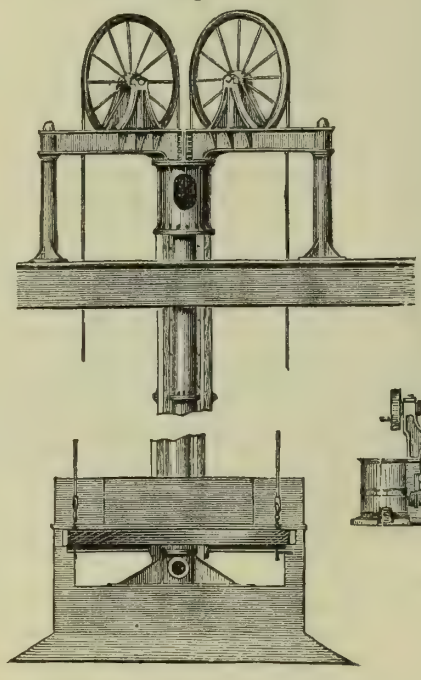
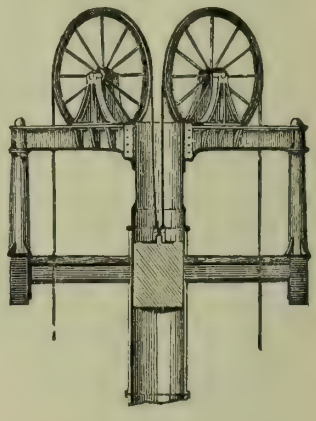
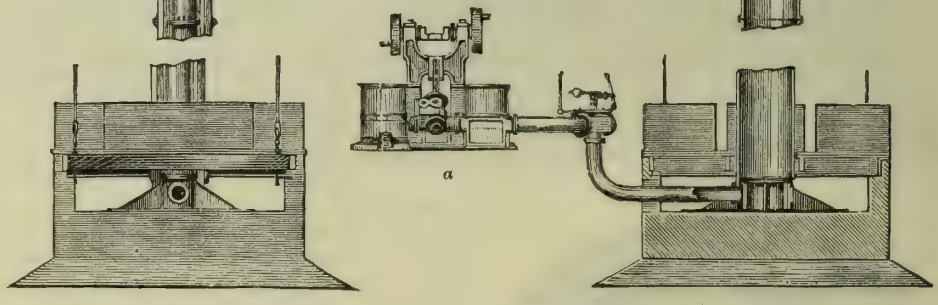
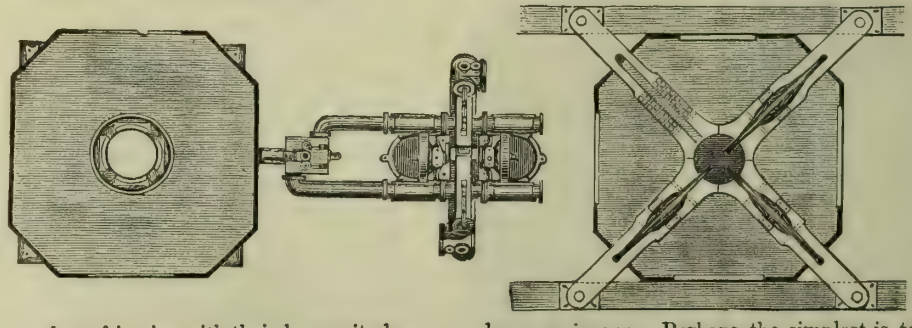


Fig. 16.





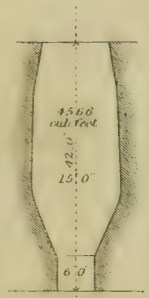


that a number of bogies with their boxes sit close up to the furnace, under separate distributing spouts at the "fall." They can then remain in place till the slag is set, and the frames can be lifted before the bogies are removed.

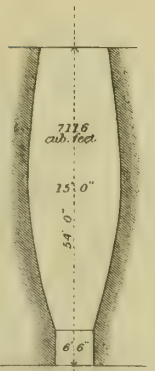
If the fluid slag be run into water it becomes granulated, and in this form can be utilized for ballast, concrete, or mortar. The calcareous slags from Bessemer pig iron form strong cements when ground up with a little fresh lime. Excellent bricks are now being largely made from blast-furnace slags. Various plans are in use. Perhaps the simplest is to grind in a mortar mill about 4 parts granulated slag and 1 part fresh lime, and mould the bricks at once. Lührmann mixes about 6 granulated slag with 1 of lime cream, in a mixing machine, and then compresses the mixture in a brick press. Bodmer mixes the finely ground slag with dry lime and some gypsum by means of a very ingenious mixing machine, slightly moistens the mixture, and compresses by hydraulic pressure. This plan, slightly modified by Wood, is now carried on largely at the

IRON.

SECTIONS OF CLEVELAND FURNACES
SHEWING GRADUAL INCREASE IN HEIGHT & CAPACITY.



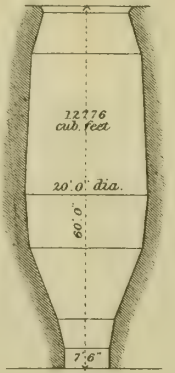
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MIDDLESBRO'
1831.
Nº 1.



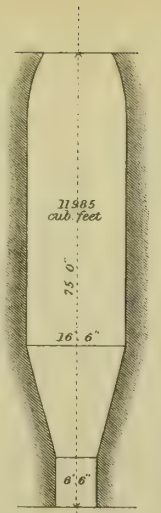
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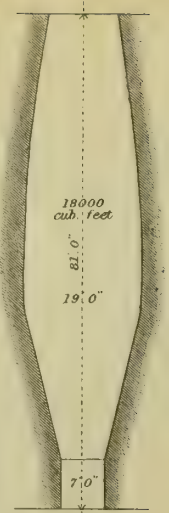
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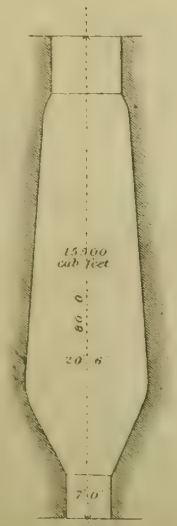
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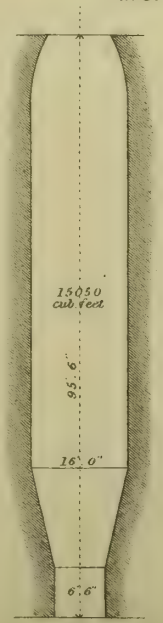
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Nº 5.



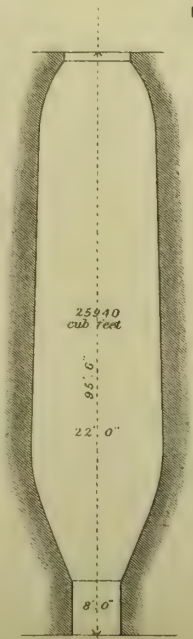
6 thus
SOUTHBANK
1864
Nº 6.



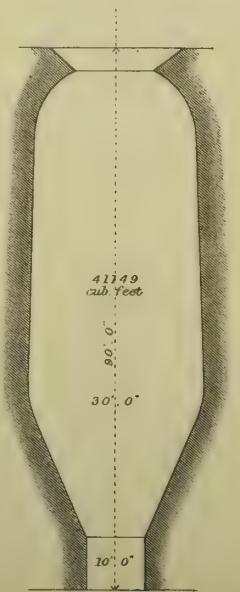
2 thus
CLARENCE
1865.
Nº 7.



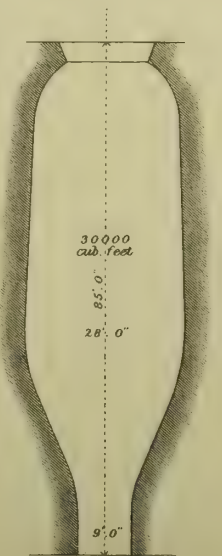
2 thus
CLEVELAND
1866.
Nº 8.



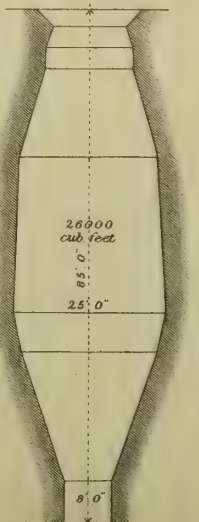
2 thus
CLEVELAND
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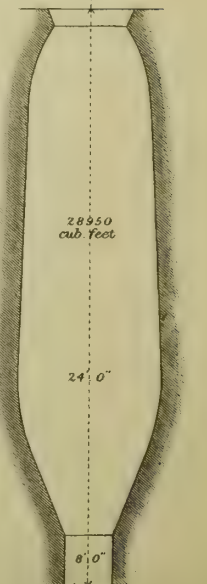
2 thus
ORMESBY
1870.
Nº 10.



2 thus
NEWPORT
1871.
Nº 11.



4 thus
AYRESOME
1871.
Nº 12.



2 thus
CLEVELAND
1871.
Nº 13.

J. B. LIPPINCOTT & CO. PHILADELPHIA.

Middlesborough slag brick-works. The Moss Bay Company merely grind up the calcareous slag to *very fine* powder, moisten it, and compress in a brick machine. Bricks made by either process harden gradually by exposure to air, and after a few weeks rival stone in hardness.

The molten iron is usually tapped from the furnace into a series of rough moulds made in sand on the pig bed. The moulds are about 4 feet long, and branch off from a general runner termed the "sow." The "pigs" (as the short castings are termed) are broken off from the sow while full red hot by forcing the point of a long bar between two of them and using it as a lever. At a red heat the iron is comparatively weak and easily broken. Each pig weighs about 1 cwt. or a little more. When cold, the pigs may be broken by dropping them across a △ shaped anvil, and the quality is judged from the appearance of the fracture. If the fracture is largely crystalline, and dark grey coloured, it is ranked as a No. 1 foundry. As the grain gets smaller and lighter in colour the grades pass to No. 2 foundry, No. 3 foundry, No. 4 forge. At this point the iron just begins to show light coloured patches, and if these are very marked it is ranked as a "mottled iron." When all traces of dark patches disappear, the iron becomes "white" iron, which is the lowest grade.

Dimensions and Makes of Blast Furnaces.—The accompanying diagram by Mr. Gjers (Plate III.) will show the changes that have taken place in the dimensions of blast furnaces in the Middlesborough district. Similar changes have gone on in other districts.

The size of a furnace must to some extent depend upon the material being smelted, and on the fuel used. With charcoal as the fuel, about 60 feet is the maximum height found to be workable. In the hematite district of the West Coast of England, furnaces from 70 to 75 feet find most favour. In this district the height is limited by the dense nature of the ore, but some economy of fuel has followed the raising of furnaces from 55 to 70 feet, while the "makes" have been proportionately increased. The greatest make of any furnace has been 803 tons in one week. In the Cleveland district, with an open calcined ironstone and good hard coke, furnaces 90 feet high work well, and although the ore is much less rich than the hematite, from 400 to 500 tons per week can be obtained from the best furnaces. The tallest furnaces are those of Ferry Hill, 103 feet high, but these, having regard to their cubic capacity, are not noted for extraordinary results.

Theory of Action of the Blast Furnace.—When oxide of iron is kept in contact with a reducing agent at a high temperature it parts with its oxygen, and metallic iron is left in a free state. The only reducing agent which is both sufficiently abundant and cheap is coal. Some kinds of coal are, however, too soft and friable to be used satisfactorily in a blast furnace; but Dud Dudley discovered that much of this soft coal, on being subjected to a partial combustion, parted with most of its volatile constituents, and the remaining carbon became baked together into a dense hard coke, which answered admirably for smelting purposes. In some cases, therefore, as in Scotland, Derbyshire, South Wales, Indiana, &c., coal is used as the reducing agent, and also as the fuel to afford the necessary heat for the process, and in most other cases coke is used. In earlier times, before the discovery of coal, and in districts where wood is plentiful even now, charcoal is often used; but as forests are of slow growth, and the consumption of charcoal for a single furnace soon clears off the growth of a century, this agent cannot compete with coal.

All iron ores are mixed up more or less with earthy matter, generally consisting of clay and quartz. The coal or coke also contains a certain quantity of the same earthy materials; and as clay and quartz in themselves are difficultly fusible, it is usual to add limestone to the charge to form silicate of lime and alumina, which is a moderately fusible body. Thus, then, the charge for a blast furnace usually consists of oxide of iron, coal or coke, and limestone for a flux. The proportions used depend upon the nature of the ore and fuel, and also upon the size of the furnace and temperature of the blast. It is usual to put the ore and limestone into one barrow, and the coke into another, to keep the weight of the fuel constant, and to increase or decrease the weight of the ore. A certain number of barrows forms a "round" or "charge." This charge is put upon the bell, and then the whole is lowered into the furnace. Thus, for a hematite furnace making Bessemer pig the charge may consist of six barrows of hematite ore of 9 cwts. each, with $1\frac{1}{2}$ cwt. of limestone on each barrow, and six barrows of coke, averaging $5\frac{1}{2}$ cwts. each. If the charge should contain an excess of silica, about a quarter cwt. of Belfast aluminous ore may be added to each barrow of ore, the object being in all cases to produce the most fusible cinder (see Table V.).

We will now follow the material through the furnace. It is understood that air, at a temperature of say 1000° Fahr., is being blown into the furnace through the twyers at the bottom, forming the "hot blast." This is forced in at a pressure of about 4 lbs. to the inch. The fuel which has reached the bottom of the furnace enters into intense combustion, but as carbon is in excess, carbonic oxide is the result. This, with the free nitrogen, passes up through the furnace, carrying heat with it, so that the material even near the top of the furnace becomes gradually raised to a red heat. But the carbonic oxide, at a temperature below this point, reduces oxide of iron, becoming itself converted into carbonic acid, which escapes from the top of the furnace. The metallic iron thus produced is left in a porous spongy state. There is, however, a further action taking place at this early stage, and a most important one. This is what is termed "carbon deposition," and the discovery of this remarkable phenomenon is due to I. L. Bell. It appears that the oxide of iron, before it is even wholly reduced, possesses the power of splitting up carbonic oxide, and retaining the carbon to such an extent that a

TABLE V.—ALUMINOUS ORES.

	Irish Ore, County Antrim.	Irish Ore from County Cavan.	Red Bay from Londonderry Co.	Aluminous Ore from Dr. Ritchie, Belfast.	Irish Ore, County Antrim, Glenarme.	From West Chester County, New York State.
Ferric oxide,	58·00	50·00	57·50	28·74	33·89	45·86
Ferrous oxide,	—	—	trace	·78	·79	
Manganese dioxide,	—	—	trace	—	—	·55
Manganous oxide,	trace	10·55	—	trace	—	—
Alumina,	17·89	7·35	22·60	41·30	39·11	39·36
Lime,	·50	·10	·78	1·70	—	·47
Magnesia,	·66	·10	·26	·23	—	7·18
Potash,	—	—	—	—	—	—
Silica,	12·50	23·00	14·90	14·05	3·82	·51
Carbonic acid,	—	1·70	—	—	—	—
Phosphoric acid,	—	—	·025	·025	—	·22
Phosphorus,	—	—	—	—	—	—
Sulphuric acid,	—	—	—	·020	—	Sulphide of Iron. 2·63
Sulphur,	trace	—	·020	trace	—	—
Titanic acid,	4·45	—	—	·30	—	2·41
Water,	6 00	5·40	3·40	13 85	21·56	1·18
Organic matter,	—	—	—	—	—	—
Total,	100·00	98·20	99·485	100 995	99·17	100·37
Total metallic iron,	40·60	35·00	40·25	20·74	24·13	34·44

piece of ore may take up nearly 4 times its weight of carbon. According to Grüner, this action can only take place in the presence of metallic iron and protoxide of iron, and the reactions are as follows: (1), $3FeO + CO = Fe_3O_4 + C$; (2), $Fe_3O_4 + CO = 3FeO + CO_2$. The reduced iron then becomes impregnated with this deposit of carbon, and as the metal travels through the furnace and gradually reaches the lower portion, or zone of fusion, it is melted in contact with the carbon, and while melting dissolves up a certain portion, so that the melted metal is no longer pure iron, but an alloy of iron and carbon. There is another element which the iron takes up in a somewhat similar manner. This is silicon. Under the influence of a powerful reducing agent, and at very high temperatures, silica is decomposed when in contact with iron, and the molten iron dissolves also a certain quantity of silicon. The quantity of carbon which the iron will dissolve is very limited, and usually varies from 2 to 4½ per cent.; but the percentage of silicon is much more variable. It may be as low as ·1 per cent., or as high as 20 per cent., or more, but usually varies from 1½ to 4 per cent. Other elements may also enter into combination with the iron; but only phosphorus, sulphur, and manganese will be considered here. Nearly all iron ores, and most fuels, contain some small quantities of phosphates. These become reduced in the blast furnace, and almost the whole of the phosphorus unites with the iron. The quantity of phosphorus in pig iron varies from mere traces up to about 3 per cent. Therefore, in making Bessemer pig for steel purposes only such ores and fuel as contain mere traces of phosphates are available. Sulphide of iron is a very common impurity in iron ores. Sulphur also exists more or less in all coal and coke, even the best Durham cokes containing from one-half to three-fourths per cent. Unlike phosphorus, however, the sulphur may be prevented to a great extent from entering the iron by using an excess of lime in the charge, and keeping the iron grey. In this case only a trace of sulphur enters the pig; but if the iron becomes white, and the slag stony or siliceous, 1 per cent. or more sulphur may easily pass into solution.

Many iron ores contain manganese, and although this element is more difficult of reduction than iron, still, if any exists in the ore, a portion will usually become alloyed with the iron.

Thus, then, the melted product of the blast furnace may contain carbon, silicon, sulphur, phosphorus, and manganese. The following series of analyses will give an idea of the average composition of different clas es of pig iron (see Tables VI. and VII.).

As has before been stated, the earthy matter of the ore and fuel unite with the flux to form a slag, which is melted by the intense heat of the furnace, and is run off into the slag bogies, to be thrown to the slag heap as a rule. Slags of necessity vary with the nature of the ores used. The following table will give an idea of their composition (see Table VIII.).

It will be noticed that slags from furnaces making Bessemer pig are white (or "grey," as they are technically called). This is due to the fact that all the iron has been reduced by the excess of fuel used, and that the slag contains an excess of lime. The excess of lime is used to take up the sulphur from the charge, and prevent it entering the iron. The sulphur appears to exist in the slag as sulphide of calcium, and when these grey slags are exposed to moist air the sulphide is decomposed, sulphuretted hydrogen and lime being formed ($CaS + H_2O = H_2S + CaO$). The slag thus becomes disintegrated, and crumbles to powder. Such slags, mixed with a little fresh lime, form quick setting cements, and bricks are now being largely made therefrom. It has been proposed to use blast furnace slags for making glass, and there seems no reason why this plan might not be carried out. These grey slags are peculiarly fitted for glass making, as they are practically free from oxide of iron, which imparts a green colour to glass.

Slags from furnaces making foundry iron are also

TABLE VI.—PIG IRONS.

	Pig Iron from Cleveland District.							Scotch.	Various Bessemer Pig Irons from West Coast.					
Iron,	93·000	—	94·24	93·04	92·91	91·41	92·36	—	93·406	93·108	93·102	93·767	94·059	93·46
Com. carbon,	·130	—	·65	·55	·36	·18	·72	—	·250	·360	·220	·180	·350	·175
Graphite,	3·000	2·70	2·15	3·00	2·40	2 80	3·05	2·60	3·550	3·530	3·366	3·430	2·570	3·320
Silicon,	1·910	1·77	1·38	1 68	2·17	3·31	1·54	1·47	2·685	2·895	2·795	2·510	2·780	2·900
Sulphur,	·090	·04	·07	·05	·11	·12	0·12	·03	·052	·052	·015	·027	·049	·003
Phosphorus,	1·780	1·00	1·27	·92	1·13	1·52	1·78	·96	·057	·055	·012	trace	·028	·034
Manganese,	not estd.	—	·69	·85	·50	·81	0·43	—	trace	trace	·490	·086	·164	·100
Arsenic,	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Copper,	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total,	99·91	—	100·45	100·09	99·58	100·15	100·00	—	100·000	100·000	100·000	100·000	100·000	100·000

TABLE VI.—PIG IRONS.—*Continued.*

	Coneygree (Staffordshire) Pig.	Derbyshire Pig.	Welsh Common White "Crystalline" Pig.	Welsh White Pig for making Common Bars.	Welsh Grey Pig for making Tin Plates.	Charcoal Pig Iron made from Lake Superior Ores.	Bessemer Iron from North Wales, made chiefly from Spanish Ores.	Pig Iron made from Tasmanian Ore. No. 1 Bessemer in fracture.	Pig Iron made from Tasmanian Ore. No. 2 Bessemer in fracture.	Swedish Bessemer Pig. (See below for Slag.)	Swedish Charcoal Pig.	Arsenical Pig Iron. Analyses by Herr Millberegger. Light Grey Pig.	White Graphitic Pig.	White Pig.	Highly Siliceous Iron.
Iron,	93·298	92·510	93·881	94·850	92·884	93·34	93·694	94·10	94·42	89 820	91·045	94·790	94·845	93·380	95·573
Com. Carbon,	·150	·36	2·310	2·512	3·130	·38	·480	·81	·94	1·950	3·342	·955	1·555	1·925	trace
Graphite,	2·505	2·753	—	—		3·39	3·160	2·54	2·14	2·15)	1·710	1·300	·880	·550	2·700
Silicon,	2·253	2·151	·895	1·091	3·238	2·28	1·580	2·33	2 15	1·390	·748	·648	·576	192	8·600
													Calcium	Calcium	
Sulphur,	·130	·016	·763	·722	·108	·03	·065	·01	·06	trace	·005	—	·050	·075	trace
Phosphorus,	·632	1·040	2·176	·567	·216	·10	·143	·07	·05	·015	·031	·440	·015	·041	·032
Manganese,	·914	1·008	·115	·201	·424	·17	·878	·14	·24	4·665	3·119	·722	·759	2·020	3·095
Arsenic,	—	—	—	—	—	—	—	—	—	—	—	1·012	1·290	1·698	—
Copper,	—	—	—	—	—	—	—	—	—	—	—	·133	·029	·110	—
Total,	99 972	99·838	100·140	99·943	100·000	99·65	100·000	100·00	100·00	100·000	100·000	100·000	99·999	99·99	100·000

TABLE VII.—SPIEGELEISEN, ETC.

	Various English Spiegeleisens.			A.U. German Spiegel.	German Spiegel.	Chromeisen.			
Iron,	75·962	72·823	76·239	84·570	86·880	9·57 *	6 88 *	10 41 *	10·0 *
Combined carbon,	5 252	3 853	4·027	5·500	4·500	2·82	2·82	4·05	3·00
Silicon,	·367	3·07	·610	·569	·625	208	2·22	—	1·00
Sulphur	free	trace	trace	trace	·038	trace	trace	—	trace
Phosphorus,	·064	·075	·092	·102	·250	·118	·03	—	·03
Manganese,	18·355	23·472	18·432	9·509	7 491	trace	trace	—	trace
Copper,	—	—	—	·047	·216	—	—	—	—
	100·000	100·540	100·000	100 297	100·000	—	—	—	—

* Chromium.

VIII. — BLAST FURNACE SLAGS.

	Various Bessemer Slags from West Coast District. (Colour Grey.)					Bessemer Slag that falls to Powder on Cooling.	Granulated Bessemer Slag that sets quickly as Mortar.	Black Slag from Bessemer Iron.	Swedish Bessemer Slag.	Green Spiegeleisen Slag.	Blue Bessemer Slag, from Barrow.	Cleveland Slag, Clarence Furnace.
Silica,	35·00	36·00	39·60	36·80	37 20	25·65	29·00	37·60	47·00	33·50	46·683	27·65
Alumina,	18 20	15·40	12·40	13·70	14·00	11·35	16·50	17·40	2·40	14·28	5·760	24·69
Ferrous oxide	—	—	—	—	—	·63	—	1·43	·45	—	1·208	·72
Manganous oxide,	—	—	—	—	—	—	—	1·04	4·46	11·64	1·062	·35
Lime,	46·03	44·79	47·50	45·45	37·64	56·35	50·55	41·50	26·75	33·65	39·168	40·00
Magnesia,	—	—	—	—	—	—	1·44	—	18 10	1·05	·987	3·55
Soda	—	—	—	—	—	—	—	—	·41	—	1·276	·99
Potash	—	—	—	—	—	—	—	—	·62	CaS_2 3·30	·967	·46
Sulphur	—	—	—	—	—	—	—	—	·011	—	2·074	1·95
Phosphoric acid,	—	—	—	—	—	—	—	—	—	trace	—	·26
Total,	—	—	—	—	—	93·98	97·49	98·97	100·201	97·42	99·194	100·62

grey, but are usually more siliceous, or "stony," than those from Bessemer iron.

When ores containing much manganese are being smelted, the slags are either green or brown. This is the case when spiegeleisen is being made. A glassy green slag indicates a healthy working of the furnace, a brown slag the reverse.

Occasionally slags are met with of a beautiful blue colour. This appears to be due to the presence of small quantities of sulphide of iron in an otherwise colourless slag. The colour can be produced at will, by running some grey slag around an iron bar. The blue slag will be formed in concentric layers around the bar. Pale pink

slags are produced when magnesia is present in the charge.

Glassy black slags are formed when insufficient fuel is used to reduce the whole of the oxide of iron in the charge, and the furnace is therefore making white iron. This kind of slag is most frequently formed when "cinder," as it is termed (slag from puddling and reheating furnaces), is used. This is not because these substances cannot be reduced perfectly. It is quite possible to make grey pig from cinder alone, but at the expense of an excess of fuel.

The worst kind of slag that can come from a blast furnace is a curly reddish-brown. It is termed a "scouring" cinder, and is caused by the ore passing through the furnace without being reduced. It merely melts and mixes with the slag. This unhealthy condition is generally the result of a "slip," as it is termed, when a mass of ore, &c., having accumulated in a certain portion of the furnace, perhaps hanging from one side, termed a "scaffold," suddenly breaks away and carries the unreduced ore at once into the zone of fusion. When started it is sometimes difficult to stop this scouring cinder, because the charge passes through the furnace so rapidly that there is no time for reduction. It has a most injurious action on the brickwork of the furnace; the slag or cinder being largely charged with oxide of iron and very basic, readily dissolves up the silica of the bricks. It is evident that such scouring cinders cause great waste of iron.

From what has been said it will be patent that the character of the slag is a point of great importance. It is, in fact, the best possible guide to the working of a furnace, the experienced eye detecting in a moment, by a glance at the slag, not only how the furnace is working, but the quality of iron which may be expected from it at the next "tap." The scientific furnace manager will carefully determine the quality of the slag beforehand, and will add such materials to the ore and fuel he is compelled to use as shall produce the most fusible slag with least waste of metal. As a rough rule a blast furnace slag should consist of about 3 silica, 2 lime, 1 alumina; but the lime must to some extent be proportioned to the sulphur present in the charge, and to the quality of iron required.

In a few exceptional cases, as in the Lincolnshire district, the gangue of the ore consists largely of carbonate of lime. In this case it is evident that silica in some form or other must be the added flux. It is usual, not to add free silica, but either an extra siliceous ore, or mill and forge cinders, which are mainly silicates of iron. In some cases, as in the Cleator district, the ores contain very little alumina, but a considerable proportion of silica. In this case an aluminous ore from the North of Ireland, near Belfast, serves as a flux to bring up the composition of the slag to the right point. Analyses of these ores will be found in the table.

Composition of the Waste Gases from Blast Furnaces.—The character of the gases evolved from blast furnaces will differ greatly according to the fuel being used, and the quality of iron under manufacture. All the nitrogen which enters the furnace as air goes off as such. Some of the moisture becomes decomposed, and small quantities of free hydrogen pass away; but the most important gases to consider are carbonic acid and carbonic oxide. Bell has found the conditions of equilibrium for these gases in the presence of metallic iron to be

Low red heat,.....	150 vol.	carbonic acid,	}	For each 100	
Full red heat,.....	47 "	"	"	}	Carbonic
Approaching white,	11 "	"	"	}	oxide.

In reducing calcined Cleveland ores the same authority maintains that when the mixed gases exist in the proportion of $40CO_2$ to $100CO$ the CO is no longer able to effect reduction in the blast furnace. Tunner has shown that in charcoal furnaces making white iron from easily reducible ores, the relative proportion of carbonic acid may be very largely increased. On the other hand, from Crossley's experiments, it appears that when hematite is being smelted the proportion of carbonic acid is decreased.

The following analyses will give an idea of the composition of the waste gases under different circumstances:—

	Cleveland Furnace.	Hematite Furnace.	Charcoal Furnace.
Carbonic acid,.....	11·75	8·36	20·9
Carbonic oxide,.....	26·62	34·97	23·81
Hydrogen,.....	·7	2·16	·39
Nitrogen,.....	60·93	54·51	54·9

It will be seen that every sample of gas contains a large quantity of carbonic oxide, and it is this gas which is available as fuel. According to the authority above quoted 48·73 per cent. of the heat-producing power of the fuel used in smelting passes off in the waste gases, in addition to the sensible heat they contain.

The following statement shows the actual heat development in the furnace, and how it is appropriated. The case refers to a furnace smelting Cleveland ore:—

HEAT UNITS DEVELOPED PER TON OF IRON.

	Centigrade Scale.
Due to oxidation of carbon,.....	81,536
Contributed by blast,.....	11,919
	93,455

HEAT UNITS ABSORBED PER TON OF IRON.

Evaporation of water in coke,.....	312
Reduction of Fe_2O_3,.....	33,108
Carbon impregnation,.....	1,440
Expulsion of CO_2 from $CaCO_3$,.....	5,054
Decomposition of CO_2,.....	5,248
Decomposition of H_2O,.....	2,720
Reduction of $P_2O_5.SO_3.SiO_2$,.....	4,174
Fusion of pig iron,.....	6,600
Fusion of slag,.....	16,720
Radiation from walls of furnace,.....	3,658
Carried off in twyer water,.....	1,818
Carried off in gases,.....	8,860
Expansion of blast, loss, &c.,.....	3,743
	93,455

Reference has been already made to the value of an increase of capacity in the blast furnace. At or about the same time that this had been demonstrated attention was drawn to the power of heating the

blast to 2000° Fahr., alleged to be possessed by the stoves suggested by Cowper, and afterwards modified by Whitwell. It was urged with some show of reason that if, by doubling the cubical contents of a furnace, the consumption of fuel had been materially reduced, why should not a corresponding saving attend a still further addition to its capacity. In like manner why, if it had been proved advantageous to increase the temperature of the blast from 600° or 700° Fahr. to 1000°, might not air of 2000° prove also beneficial.

These two important questions were treated as follows by I. L. Bell. This author proved, experimentally, that oxide of iron was susceptible of reduction by carbonic oxide at a temperature much below that described by previous writers as being required for the operation. In a very few minutes, therefore, after the ore is shot into the throat of the blast furnace reduction begins, and in most cases before it has travelled 12 or 13 feet downwards this division of the process may be said to be completed. Below this level, omitting any chemical action connected with the formation of cyanogen salts, the value of height in the furnace must only be regarded as a means of intercepting the heat, which is carried upwards by the rapid current of gases generated by the combustion of the fuel of the twyers. These gases arrive speedily at the point of exit, and in the event of the furnace not being of sufficient height, they carry with them, in the form of sensible heat, the useful effect of a considerable portion of the combustible employed in the operation. In a furnace of 48 feet in height the loss from this cause was found by Bell to amount to 16 per cent.

In a furnace 80 feet high, with a capacity of 12,000 cubic feet, Bell found that something like 9 per cent. of the heat evolved in the furnace was carried off in the escaping gases, which had a temperature of something like 600° Fahr. Instead of there being any material reduction in the loss arising from this cause, he found that the gases left a furnace with a height of 80 feet and a capacity of 26,000 cubic feet as hot as they did from one of less than half the size. This, be it remembered, took place although the time the ascending stream of gas was in contact with the descending current of solids was greatly increased, inasmuch as the work performed by the larger furnace was, having regard to the relative sizes of the two, 35 per cent. less than that of the smaller.

This constancy of temperature in furnaces above a certain capacity was shown, experimentally, to be due to the deoxidation of the ore being attended by an actual increase of temperature. Under these circumstances, and as the change must always take place near the top of the furnace, any further addition to the height was followed by a corresponding removal of the zone of reduction from the hearth.

A second source of loss, and which has already been alluded to in low furnaces, was the elevated temperature of the upper or reducing zone. As formerly stated, the product of the action of carbonic oxide on oxide of iron is carbonic acid; but if the the last named compound of carbon and oxygen meets carbon at a full red heat carbonic oxide is again formed ($CO_2 + C = 2CO$). This reaction is not only attended with a loss of heat, but so much carbon as would otherwise reach the twyers is dissolved within a few feet of the top, and represents so much waste.

The action of carbon deposition, also already referred to ($2CO = CO_2 + C$), is also one of a heat evolving character of itself, and besides, has the advantage of returning carbon to the zone of combustion at the twyers. Moderate temperatures are best suited for this action; indeed, at a bright red heat the action is all but suspended.

The correctness of these views regarding the inexpediency of raising the height of the furnace beyond 80 feet has been confirmed by no gain having resulted from going beyond this altitude.

Owing to the generally spread belief that the heat of the hot blast possessed some virtue peculiar to itself, it was more difficult for iron-masters to satisfy themselves that the advantages it afforded at the less elevated temperature of about 600° Fahr. would not, practically at all events, hold good up to 2000°. It was a favourite argument to point out that, after making proper allowance for collateral benefit derived from heating the blast, as Neilson obtained it, 8 cwts. of coal burnt in the hot air apparatus saved 30 cwts. of coke in the furnace. Surely, therefore, some approximation must hold good were the air heated to double this, or 1200° Fahr. Bell's contention is, that there is no mysterious virtue in the heat conveyed into the furnace with the air that drives it, and that the very same effect may be, and has been, secured by a mere addition to the dimensions of the furnace, without heating the blast.

By making the air a vehicle of conveying a portion of the heat into the hearth, the volume of gases passing through the furnace for a given amount of duty performed is reduced. This, in other words, is equivalent to an increase of its effective capacity twice in the various reactions, constituting an important element. So far, there does not appear any reason why, under any condition, a given number of heat units contained in the hot blast should not be as effectual as the same number evolved by the combustion of the carbon in the hearth, and that, therefore, the one might be indefinitely replaced by the other. Doubtless, were the sole operation of the blast furnace one of the mere application of heat to effect fusion, it would be immaterial how this heat were produced. This, however, is not so, for in the upper zone regard has to be had to the conditions required for the proper performance of the reduction of the ore, which is essentially dependent on chemical action. This, as has already been said, consists in the power carbonic oxide has of robbing oxide of iron of its oxygen. This power, however, is not unlimited; and according to Bell, as soon as one-third of the carbon in the gases has passed into the state of carbonic acid further action as a reducing agent is suspended. The quantity of heat absorbed by the operation is such that, of the total quantity

required, something like 13 per cent. may be supplied by the hot air before the oxidation of the gases, by the reduction of the ore, has converted one-third of the carbon into carbonic acid.

An estimate based on the conditions described in the foregoing observations brings out the maximum quantity of the best South Durham coke required for smelting a ton of iron from Cleveland stone, containing 42 per cent. of iron in its calcined form, at about 20½ cwts.; and according to the writer's opinion, this is as easily done in a furnace containing 15,000 cubic feet driven with air of 1000° Fahr., as it is in one of double the size with blast at 1500° Fahr.

Spiegeleisen and Ferro-manganese.—Compounds of iron and manganese, containing from about 7 per cent. manganese and upwards, have usually a silvery white fracture and largely crystalline structure. Hence the term spiegeleisen, or looking-glass iron. This class of iron is easily produced whenever the ore contains sufficient manganese. Until MUSHET discovered the value of such an alloy as an adjunct to the Bessemer process, it was only made as it were accidentally, and only valued for the iron it contained. BESSEMER soon saw the value of the manganese in his process, and instigated HENDERSON of Glasgow to produce an alloy much richer in manganese than any that had hitherto been made in the blast furnace. This he did by reducing carbonate of manganese in a Siemens furnace, and melting it up with a small portion of pig iron. The product was very rich in manganese, and was termed ferro-manganese. For a long time it was assumed that these rich alloys, containing 30 per cent. and upwards of manganese, could not be made in the blast furnace; but since the introduction of the highly manganiferous ores of the south of Spain (see Table IX.) for spiegel making, the manufacturer has gradually discovered that manganese can be reduced and melted in the blast furnace with nearly the same ease as iron. Hence ferro-manganese of very good quality is now a regular blast furnace product, although the highest alloys, containing up to 75 per cent. manganese, are still made according to HENDERSON's plan.

In making spiegel and ferro-manganese in the blast furnace, care must be taken to have sufficient silica in the charge to flux away a portion of the manganese so as to make a fluid slag. For this reason the burden of fuel must not be so great as to reduce the whole manganese to the metallic state. A greater quantity of coke is required for making spiegeleisen than for ordinary foundry pig, in consequence of the greater difficulty of reduction. This is the case also when very siliceous pig is required. There is every probability of highly siliceous and highly manganiferous iron becoming far more important to the steel maker than they have hitherto been. Compounds of iron and chromium are also likely to be useful in the manufacture of special kinds of steel. At present these are partly produced in the blast furnace and partly in the crucible. In order to obtain a more intimate mixture between the coke and the ore, so as to facilitate reduction, the plan has been tried of grinding up the ore with small coal, and coking the mixture, thus producing a metalliferous coke, which is used alone for the blast furnace charge.

The importance of these new alloys renders it desirable that some systematic terms should be used to designate them. It would be convenient to name the alloy of iron and manganese, manganeisen; of iron and chromium, chromeisen; while the triple alloy of iron, silicon, and manganese might be termed mangan-silicon-eisen.

TABLE IX.—MANGANIFEROUS ORES.

	Manganiferous Ore from Crossfell, England.	Garrucha or Palamores BlackSpanish).	Manganese Ore from North Coast of Spain, near Bilbao.	Manganiferous Ore from Onolana Mine, near Carthagena.	Manganiferous Ore from Isidoro Mine, near Carthagena.	Manganiferous Ore from Carthagena.	Manganiferous Ore, shipped at Carthagena.	Manganese Ore, shipped at Porman.
				Iron.	Iron.			
Ferric oxide,	65·90	77·23	—	33·50	27·50	48·25	48·57	39·57
				Oxygen.	Oxygen.			
Ferrous oxide,	—	—	trace	19·75	20·77	—	—	—
Manganese dioxide,	6·45	14·04	80·820	—	—	25·41	29·47	21·20
				Manganese.	Manganese.			
Manganous oxide,	—	—	—	17·21	22·31	—	3·46	3·06
Alumina,	1·00	1·85	—	3·20	4·80	2·33	3·34	3·65
Lime,	trace	—	—	2·84	2·98	1·60	2·00	7·00
Magnesia,	trace	1·50	—	—	—	·43	1·05	1·58
							BaO.	BaO.
Potash,	—	—	—	—	—	—	·64	·59
	Res.							
Silica,	13·00	2·00	13·700	6·50	·5·65	11·35	10·80	11·15
Carbonic acid,	—	—	—	—	—	—	1·55	5·50
Phosphoric acid,	·178	·25	·214	—	—	·08	·05	·08
Phosphorus,	—	—	—	—	—	—	—	—
Sulphuric acid,	—	—	—	—	—	—	—	—
Sulphur,	trace	·14	—	1·32	·62	·09	·04	·03
				Zinc.	Zinc.			
Titanic acid,	—	—	—	·57	trace	—	—	—
Water,	12·70	3·24	7·300	not est	imated	9·80	6·00	5·90
							ZnO.	ZnO.
Organic matter,	—	—	—	—	—	—	2·90	·50
Total,	99·228	100·25	102·034	84·89	84·63	99·34	99·85	99·81
Metallic iron,	46·13	54·06	—	—	—	33·78	24·35	25·70
" manganese,	—	—	51·12	—	—	—	20·43	14·65

Fume from Blast Furnaces.—A very large quantity of dense white fume is noticed to escape from the tops of blast furnaces, along with the escaping gases. In the case of a Cleveland furnace, I. L. Bell has estimated that 2·6 cwts. of fume were sometimes escaping for every ton of metal produced. The following analyses will explain the nature of this substance: 29 grains were collected from 1 cubic mètre of gas of which 14·78 grains were soluble in water.

	Soluble in water.		Insoluble in water.
Loss on heating,	10·46	....	—
Silica,	1·37	....	11·00
Alumina with trace Fe_2O_3,	12·2	....	10·76
Lime,	trace	....	2·06
Magnesia,	trace	....	trace
Chlorine,	·57	Carbonic acid,	7·00
Sulphuric acid,	·59	....	—
Zinc oxide,	4·58	....	13·28
Carbonates of potash and soda,	22·90	....	3·07
	52·67	....	47·17

Production of Malleable Iron from Cast Iron.—One of the most simple plans, though one of the latest in chronological order, consists in embedding the cast iron in powdered oxide of iron, and subjecting the whole to a moderate but long continued heat. This process is somewhat similar in character, though reverse in its action, to the old cementation process for making steel. The plan is not applicable to large quantities of material, or to large masses; but is much used for making what are called *malleable castings*. The small castings are embedded with oxide of iron in cast-iron chests, and six or eight of these chests are placed in a furnace. Sometimes they are placed on the bed of an ordinary reverberatory furnace. A better plan is to place them upon a rotating bed. They are kept at a bright red heat for five or six days, and then gradually cooled. The following analyses of two samples (about a quarter of an inch thick), before and after annealing, will show what influence the process has upon the impurities in the iron. The unannealed castings, when broken, showed a white fracture, all the carbon being in the combined state. It is important to have the carbon in this state.

CASTING I.

	Before Annealing.	After First Annealing.	After Second Annealing.
Silicon,	·445	·438	·449
Phosphorus,	·315	·327	·315
Manganese,	·529	·585	·525
Sulphur,	·059	·067	·083
Total carbon,	3·43	1·51	below ·10

CASTING II.

	Before Annealing.	After First Annealing.	After Second Annealing.
Silicon,	·585	·614	·614
Phosphorus,	·280	·290	·295
Manganese,	·585	·616	·575
Sulphur,	·105	·147	·162
Total carbon,	3·48	·43	below ·100

From the above it will be seen that the carbon is thoroughly oxidised and removed, while no reduction takes place in the absolute quantity of the other elements; indeed the sulphur slightly increases. This is probably due to the absorption of the sulphur given off by the fuel. It is important that the iron be fairly free from silicon, phosphorus, and sulphur, otherwise the castings become very weak after annealing. When the casting is moderately thick it would appear that while the carbon near the surface may have been removed, that in the interior may become altered from combined to graphitic carbon, thus producing what is technically termed "black heart."

Sometimes the annealed castings become very brittle from some at present obscure cause. The following analyses of specially weak and very tough specimens, seem to favour the idea that weakness may result from absorption of oxygen (as in the Bessemer process) after the carbon has been all removed.

VERY WEAK SAMPLE.

	Once Annealed. Large Crystalline Facets.		Twice Annealed. Crystalline Facets extending right across Fracture.
Silicon,	·450	.....	·589
Phosphorus,	·266	.....	·212
Manganese,	·223	.....	·153
Sulphur,	·139	.....	·105
Carbon,	·10		none or slightest trace.

VERY TOUGH CASTING.

Could be bent cold through angle of 90° without fracture.

Silicon,	·719
Phosphorus,	·204
Manganese,	·270
Sulphur,	·036
Carbon,	1·842

The oxide of iron used in the process gradually loses its power, and becomes exhausted even when only reduced to the state of ferrous oxide, as will be seen from the following analysis of spent ore from making malleable castings:—

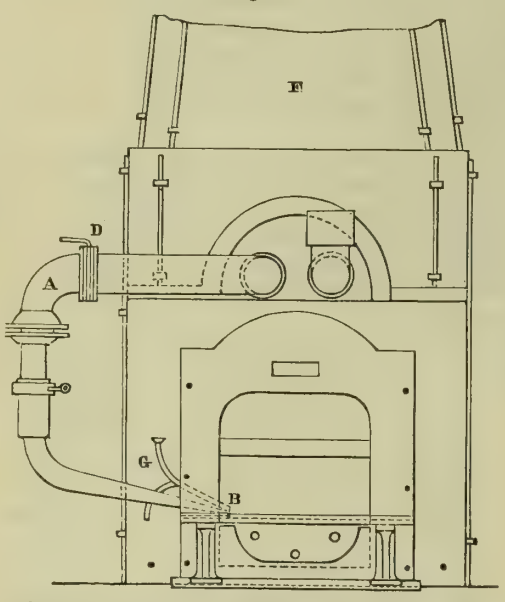
Ferric oxide (Fe_2O_3),	75·09
Ferrous oxide (FeO),	5·14
Manganous oxide (MnO),	·23
Alumina,	1·92
Lime,	2·39
Magnesia,	·52
Silica,	14·43
Sulphur,	·04
Phosphoric acid,	·08
Moisture,	·04
	99·93
Metallic iron,	62·00

The manufacture of small articles requiring considerable strength is now largely carried on by this plan, but it is not applicable to articles that require subsequent forging.

Probably the oldest method of producing malleable or wrought iron from cast iron, consisted in melting the pig iron in a *finery* or hearth in contact with the fuel, but exposed to the oxidising action of a blast of air. Charcoal was the fuel employed. By this means the iron was first melted, and then the carbon and silicon burnt out, leaving a pasty lump of iron in the hearth. In order to insure perfect oxidation of the carbon and silicon, the iron

was lifted from time to time into the blast until the whole became pasty, when the ball was removed,

Fig. 17.



and hammered under a tilt hammer into rough bars. Various modifications of this plan were adopted in different countries; but all with the same object in view, and having the same general plan of working.

The plan in its most perfect state is still used in Sweden, under the name of the Lancashire hearth process. Figs. 17, 18, and 19, taken from Dr. Percy's work, illustrate the furnace and mode of working — A, blast pipes; B, twyer; C, hearth; D, valve; E, table; F, stack; and G, water pipes.

Manipulation.—All being in working order, and the ball obtained in the last heat removed, &c., charcoal dust is spread out on the foreside, and the hearth is filled with clean charcoal. The pig iron, which is in plates 2 or 3 inches thick, and has been previously heated on the plate in the flue, is transferred to the hearth, the charge being 200 lbs. Fresh charcoal is added and the blast turned on, when in about half an hour the metal will have completely melted down, and in dropping through the blast from the twyer have become partially oxidised. By the action of the oxide of iron thus formed, and of the basic silicate of ferrous oxide remaining in the hearth at the close of the last operation upon the molten pig iron, the latter is decarburized to a considerable extent, and in consequence becomes less fusible and more pasty. After perfect fusion of the metal the refining proper begins. This consists in incessantly breaking up the metal with an iron bar, and carrying towards the twyer the raw portions, which, being more highly carburized and more fusible than the rest, always run down to the bottom, and there harden. The metal, which has thus more or less solidified, is broken up and submitted to the action of the blast until all is sufficiently refined: this operation lasts about half an hour. Subsequently all the metal is brought up to the top of the hearth, and again heated to form the ball; fresh charcoal being thrown into the hearth, and the unmelted portions being kept up at intervals with an iron bar, to prevent their adhering to the ball before having been melted.

Fig. 18

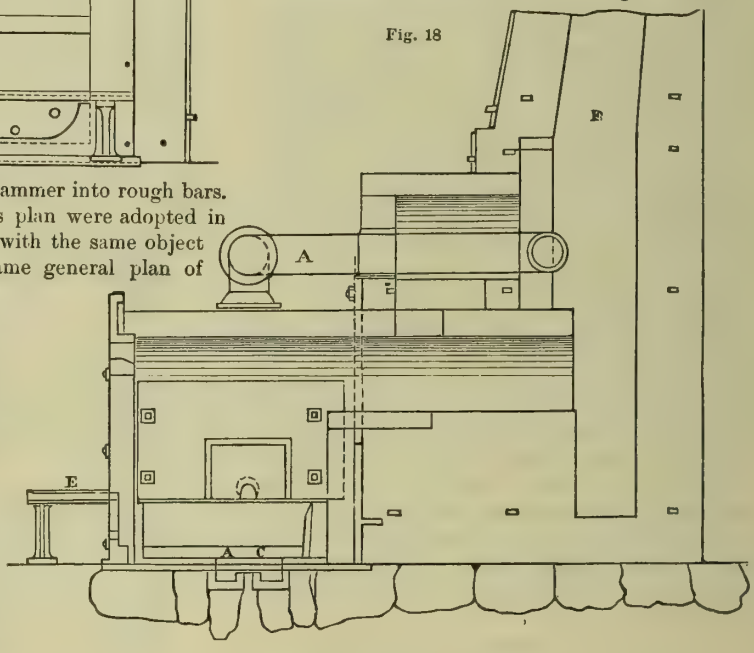
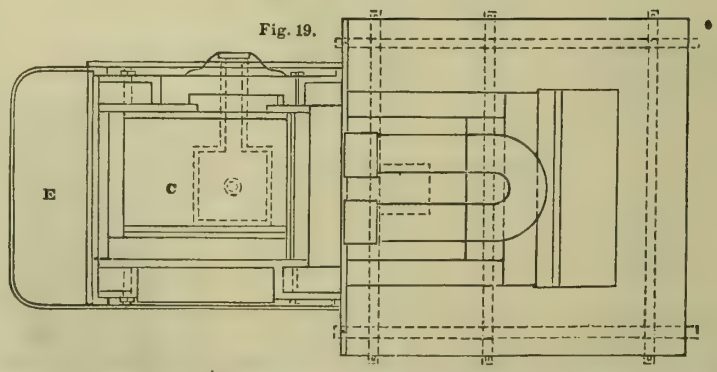


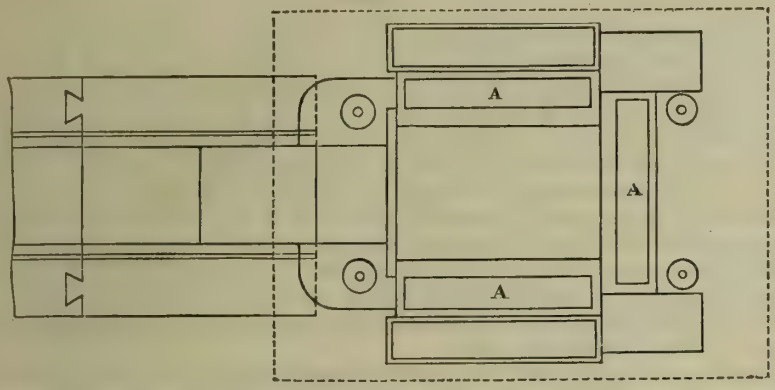
Fig. 19.



The ball is then taken out, and hammered into a prismatic shape, which is cut into pieces to be welded

in another fire. The whole process lasts from an hour and a quarter to an hour and a half.

Fig. 20.



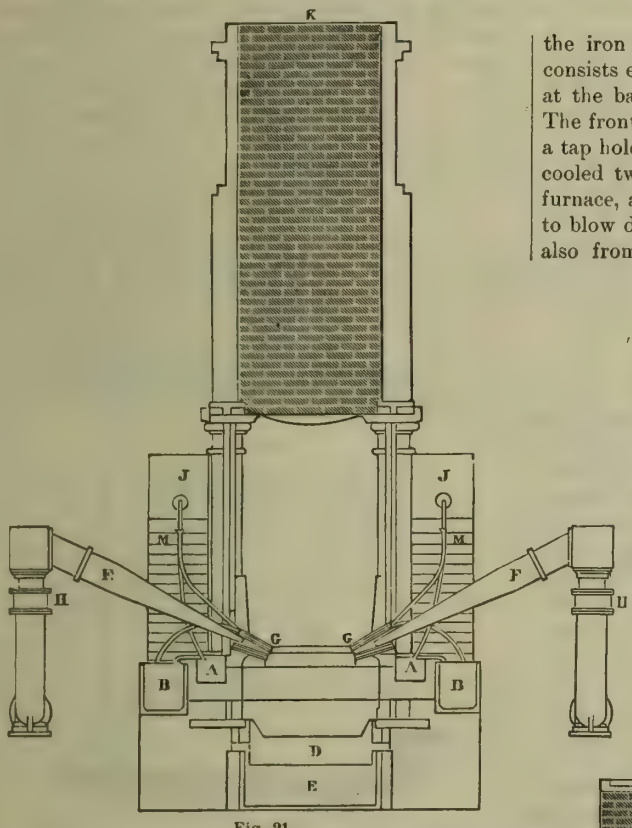


Fig. 21.

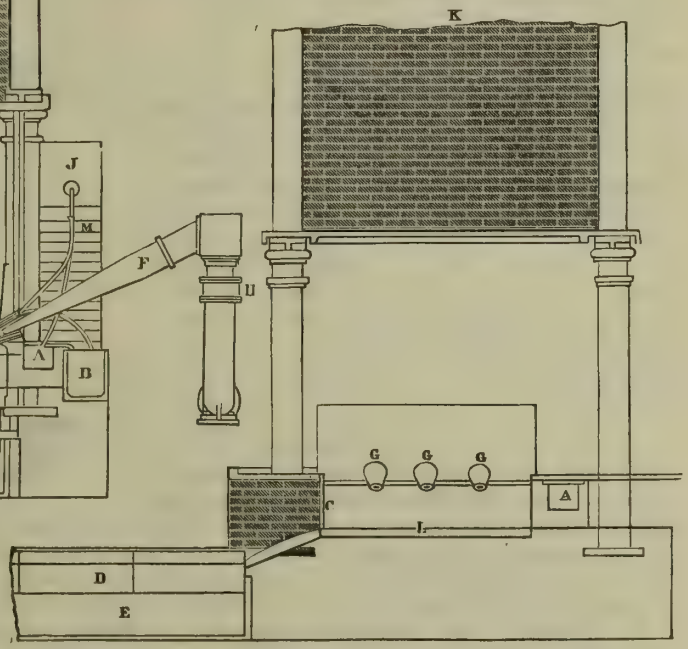
The blast is frequently used at a temperature of 100° C., and at a pressure of $2\frac{1}{2}$ inches of mercury.

The cut up pieces to be drawn out under the hammer are welded and heated in hearths much resembling in size and construction the charcoal finery itself; but the furnace now most extensively used for this purpose is the gas-welding or reheating furnace invented by G. Ekman.

The production of wrought iron by these means is costly, on account of the small quantities that can be manipulated, and the great waste of iron during the operations. But the quality of the product is excellent, even when inferior pig has been used.

During the process of melting down pig iron a certain amount of refining takes place, even in a cupola; and this action goes on to a much larger extent in the melting down in an open hearth. By continuing the blast from inclined twyers the refining is still further promoted, even though the iron be left in the hearth. Hence the refinery, or running out fire, was much used in South Wales for preparing the iron for the puddling process. The refinery consists essentially of a rectangular hearth inclosed at the back and sides by water-cooled iron blocks. The front is formed by a solid cast-iron plate with a tap hole in the bottom. One, two, or three water-cooled twyers are inserted through the sides of the furnace, and inclined at an angle of about 30°, so as to blow down upon the iron. Figs. 20, 21, and 22, also from Dr. Percy, represent a refinery at the

Fig. 22.



Bromford Iron Works—A, hollow sides of cast iron; B, water troughs of cast iron; C, dam plate; D, running out bed of cast iron; E, water box; F, blast pipes; G, twyers; H, valve; J, water tank; K, stack; L, flat bottom; M, water pipes.

The operation is carried on as follows:—The fire being lighted and the hearth partially filled with coke

a charge of about a ton of pig iron is piled upon the coke. Fresh coke is thrown over the whole and the blast turned on. In from one to one and a half hour the whole of the pig iron has been melted, but the blast is continued for about half an hour longer. The refiner judges from the character of the pig the amount of refining required, but ascertains when the operation is complete by the appearance of the cinder and iron which he brings out by means of a long iron bar. The metal and cinder are then tapped out together, and run into a water-cooled cast-iron bed. Water is thrown over the whole, which chills the iron and promotes the separation of the cinder. The slabs of metal are then removed from the chills by hooks suspended from a pair of large wheels, and broken up by a double-handled sledge.

It requires about 4 cwts. of coke to produce 1 ton of refined metal. Formerly at Dowlais, the metal was run direct from the blast furnace into the refinery, thus saving some fuel, and quickening the process. The refinery forms a convenient means of melting up heavy masses of iron, such as old rolls, &c., which can be pushed forward into the furnace as they melt down.

The pressure of the blast is generally from 2 to 3 lbs., and is usually taken from the same mains that supply the blast furnaces. The action is at all times an oxidising one, and hence there is considerable loss of iron in the process, varying from 8 to 15 per cent.; but if the blast be allowed to impinge too directly on the iron, it may become much greater.

The refining can be carried out to any extent; but if pushed too far, the iron becomes over-refined, and full of honeycomb. The object is to burn out the greater portion of the silicon. If carried out properly, the refined iron is solid, bright on fracture, with an almost silvery appearance. It approaches in character to hard steel. The following analyses will show the character of the change that takes place:—

	Dowlais White Pig Iron.	Refined Metal from same.
Iron,	94·006	96·485
Carbon, { graphite, ·8 / combined carbon, 1·797 }	2·597	2·428
Silicon,	1·908	·128
Sulphur,	·553	·144
Phosphorus,	·886	·815
Manganese,	·050	trace
	100·000	100·000

The slags produced in this process are generally more free from phosphorus than those from the charcoal finery (when using the same iron); but, like them, contain a large quantity of iron, as will be seen from the following analysis of a sample such as would be produced when refining the above pig:—

Silica,	33·33
Ferrous oxide,	54·94
Manganous oxide,	2·71
Alumina,	5·75
Lime,	1·19
Magnesia,	·50
Sulphide of iron, { iron, / sulphur,	·17 / ·10
Phosphorus,	·99
Copper,	traces
	99·68

From the above analyses it will be seen that while the carbon is very slightly reduced absolutely, the silicon and sulphur are largely eliminated, but phosphorus is only very partially removed. It must be borne in mind that a considerable waste of iron goes on in the process; so that although the per cent. of phosphorus in the sample of refined iron is nearly as high as in the pig, the absolute quantity has been reduced, and some has passed into the slag.

Twenty or thirty years ago the refining process was largely used, particularly in Wales. There and elsewhere it has been all but discontinued, and pig iron without any preliminary treatment is employed in the manufacture of malleable iron. Some of the best brands, particularly those known as best Yorkshire, are almost exclusively made from refined metal.

Puddling.—Since the time of Cort the process of puddling has gradually been improved, until it has practically superseded all other modes of making wrought iron in large quantities. The essential difference between puddling and the modes of producing wrought iron just considered, consists in the separation of the metal in the puddling furnace from all contact with the fuel. Thus a commoner fuel can be employed without injury to the iron.

Description of a Puddling Furnace and the Mode of Working.—It consists of a fire-place in which the fuel is burnt, a reverberatory chamber in which the metal is treated, and a chimney to create the necessary draught, with a damper for regulating it. Figs. 23, 24, and 25 show the construction of an ordinary puddling furnace:—Fig. 23 is an end view of fire place; Fig. 24 is a sectional plan along the line C—D,

Fig. 23.

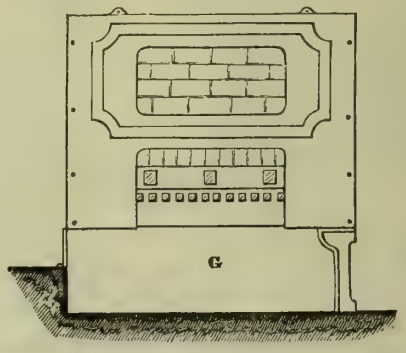
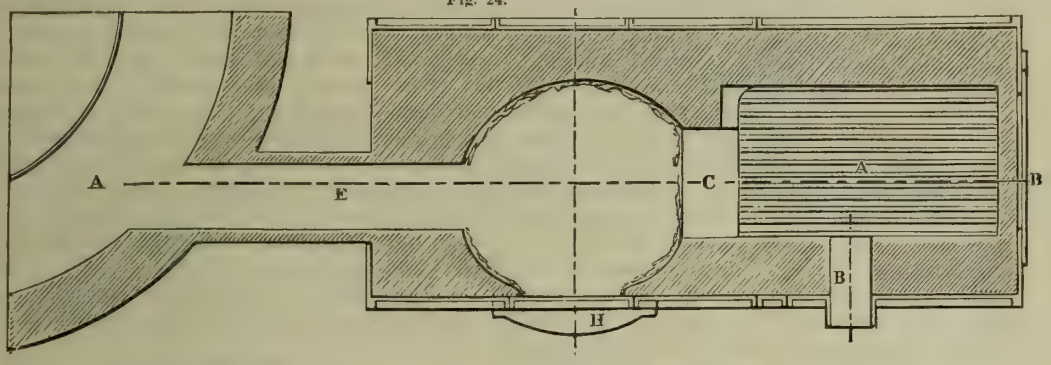


Fig. 25; and Fig. 25 is a sectional elevation along the line A—B, Fig. 24. A is the furnace; B, charging door for coal; C, bridge; D, puddling chamber; E, fire bridge; F, Rastric boiler; G, ash pit; H, working door. The pig iron is placed upon the bed of the furnace and gradually melted down. The workman then, with a long hooked iron bar, termed a "rabble," continually agitates the bath of metal, so as to expose fresh portions to the action of the lining of the furnace, and to the hot gases passing over the surface. He thus mixes the whole up, and prevents one portion from becoming refined before another. When all the iron has been melted the damper is usually

put down for a while, to keep down the temperature of the metal to the point most favourable for producing the "boil," as it is termed. This is a violent ebullition which takes place shortly after the

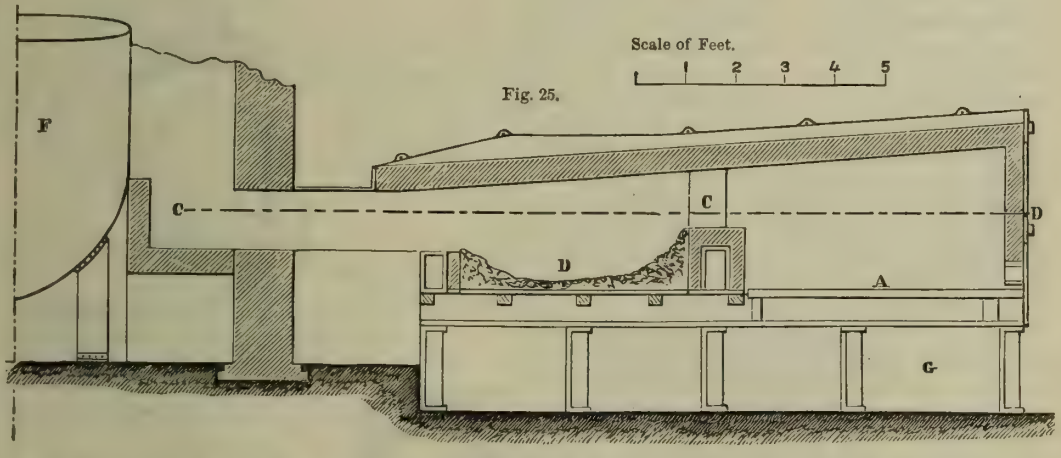
Fig. 24.



Scale of Feet.

1 2 3 4 5

Fig. 25.



whole has melted, and is due to the escape of carbonic oxide, formed by the oxidation of the carbon. This appears to take place most violently directly after the bulk of the silicon has been burnt out. Hence it comes on more quickly after melting, when white iron is under treatment, than when the pig is grey.

Soon after the boiling is over the metal loses its fluidity, and pasty masses are formed. The metal is then said to be coming "to nature," or "dropping." Up to this point the work of agitating the metal, or "rabbling," is generally done by the "under-hand." The "fore-hand" now takes his turn, and pushes back the more advanced portions, and brings forward the remainder. He then gathers the whole into one mass, and afterwards divides it into separate "balls," which are quickly drawn from the furnace and "shingled" under a squeezer or a hammer.

In reference to this process I. L. Bell has recently given the result of some experiments in a paper read before the members of the Iron and Steel Institute. A careful examination of the various processes connected with the manufacture of iron, and with the conversion of pig iron into steel by the Bessemer process, led him to infer that by keeping molten cast iron in contact with oxide of iron at a low temperature, nearly the whole of the phosphorus can be removed before the carbon is greatly reduced in quantity. Should his expectations be realized, we may hope, from pig such as that of Cleveland, to obtain a material which at present can only be produced by using ores comparatively free from phosphorus.

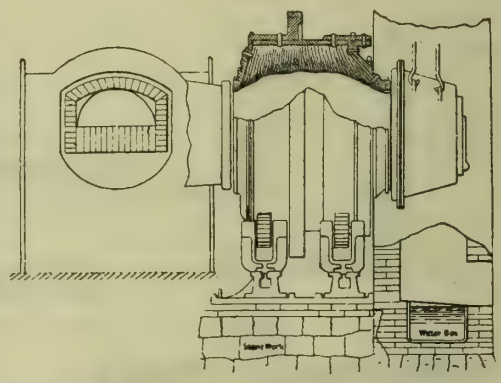
Theory of the Process.—The reactions taking place in the puddling furnace are essentially those due to oxidation. The agents of oxidation may be the free oxygen of the heated gases passing over the metal, or fluid oxygen in the form of oxide of iron. Formerly the effect of the oxide of iron was lost sight of, but now it is clearly demonstrated that either ferric oxide or magnetic oxide are capable of giving a portion of their oxygen at a high temperature to combine with the carbon, s licon, sulphur, and phosphorus existing in the pig iron, and thus remove them. It is therefore found advisable to line, or, as it is termed, "fettle," the puddling chamber with rich oxides of iron. Portions of this lining become melted with the iron, and form a bath of cinder in which the fluid iron is agitated. Inasmuch as it is impossible to get absolutely pure oxide of iron, some silica being always present, and as this is increased by the melting of the bricks in the roof of the furnace, the bath is usually of varying composition, but

it is always highly basic; and hence as the silicon, sulphur, and phosphorus are oxidised to their respective acids, these are neutralized and combined with the oxide of iron in the bath, and are thus removed to a great extent. It is possible that some sulphur and phosphorus may be removed as gaseous products. The carbon is oxidised to carbonic oxide, jets of which may be seen burning with a blue flame all over the bath at a certain period in the process. As the carbon, silicon, &c., are removed the iron becomes less fusible, and assumes the condition of a pasty mass. In this condition the particles of iron possess great power of cohesion when brought into intimate contact. They thus stick together, or become "welded," as it is termed. Welding then consists in the union of two pieces of iron by virtue of cohesion, and perfect welding can only take place when the surfaces are absolutely clean. Whatever, therefore, tends to free the surface of iron from all foreign matter promotes welding. Thus a reducing atmosphere in which any scale of oxide of iron becomes reduced to the metallic state, or a flux which will dissolve up such scale and leave a fluid slag that can be squeezed from between the metallic surfaces, promotes this operation. The puddled iron that has been gathered together in the furnace into a ball is of so spongy a nature that it is full of such a fusible slag; and when the ball is brought to the hammer or squeezer this fluid slag is easily expressed, and the iron welded into a solid mass.

From what has been said it will be gathered that the sides and bottom of the furnace require to be constantly renewed or "fettled," and such is the case. Any rich iron ores free from silica serve for this purpose, and also iron scale and "tap cinder," as it is termed, which is nearly pure oxide of iron formed by the oxidation of metallic iron during the process of heating. Frequently scrap iron is intentionally oxidised in the puddling furnace to produce fettling. When sulphury pig is being puddled manganese ore is found to be a valuable fettling material, on account of its great affinity for sulphur. The various nostrums advocated as "physic" for the puddling process generally include more or less manganese oxide; but in order to be efficacious the material must be used in sufficient quantity, far in excess of what theory would point out.

The manual labour demanded from the puddler is so excessive, that for years the attention of inventors has been devoted to the discovery of some means for performing the operation mechanically. Tooth was one of the first to suggest a fairly practicable puddling machine; but after years of labour and much patient investigation, Menelaus had nearly given up hope of success when Danks of Cincinnati showed that, by using oxide of iron as the lining material, and in an improved form of Tooth's apparatus, very satisfactory results were produced. The statements made by Danks were fully corroborated by a commission sent out to America by the Iron and Steel Institute; and although the first attempts to use his revolving puddling furnace in England disclosed many difficulties yet to be overcome, it may now be confidently asserted that the problem of mechanical puddling is fully solved. Messrs. Hopkins & Gilkes, of Middlesborough, are at present constantly running six of these rotating furnaces, day and night, and producing nearly 5 tons per shift out of each furnace, while the production of an ordinary hand-furnace is only about one-fourth this quantity. At present mechanical puddling scarcely affords any advantage in point of economy over hand work; but this is due to defects in the designs of the machinery, which will doubtless be rapidly remedied. The iron produced, however, is far superior to that from hand-worked furnaces, and there is also an advantage in point of yield. Plate IV. will sufficiently explain the construction of the Danks' revolving furnace, while Figs. 26 and 27 show

Fig. 26.



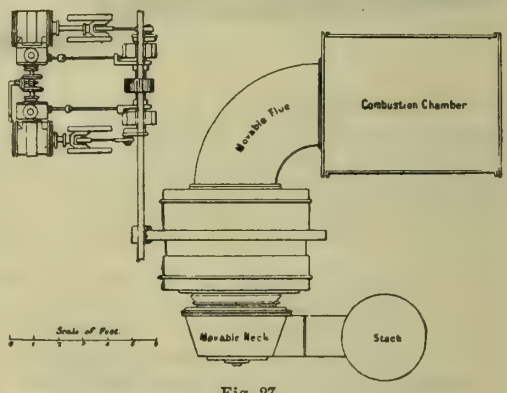


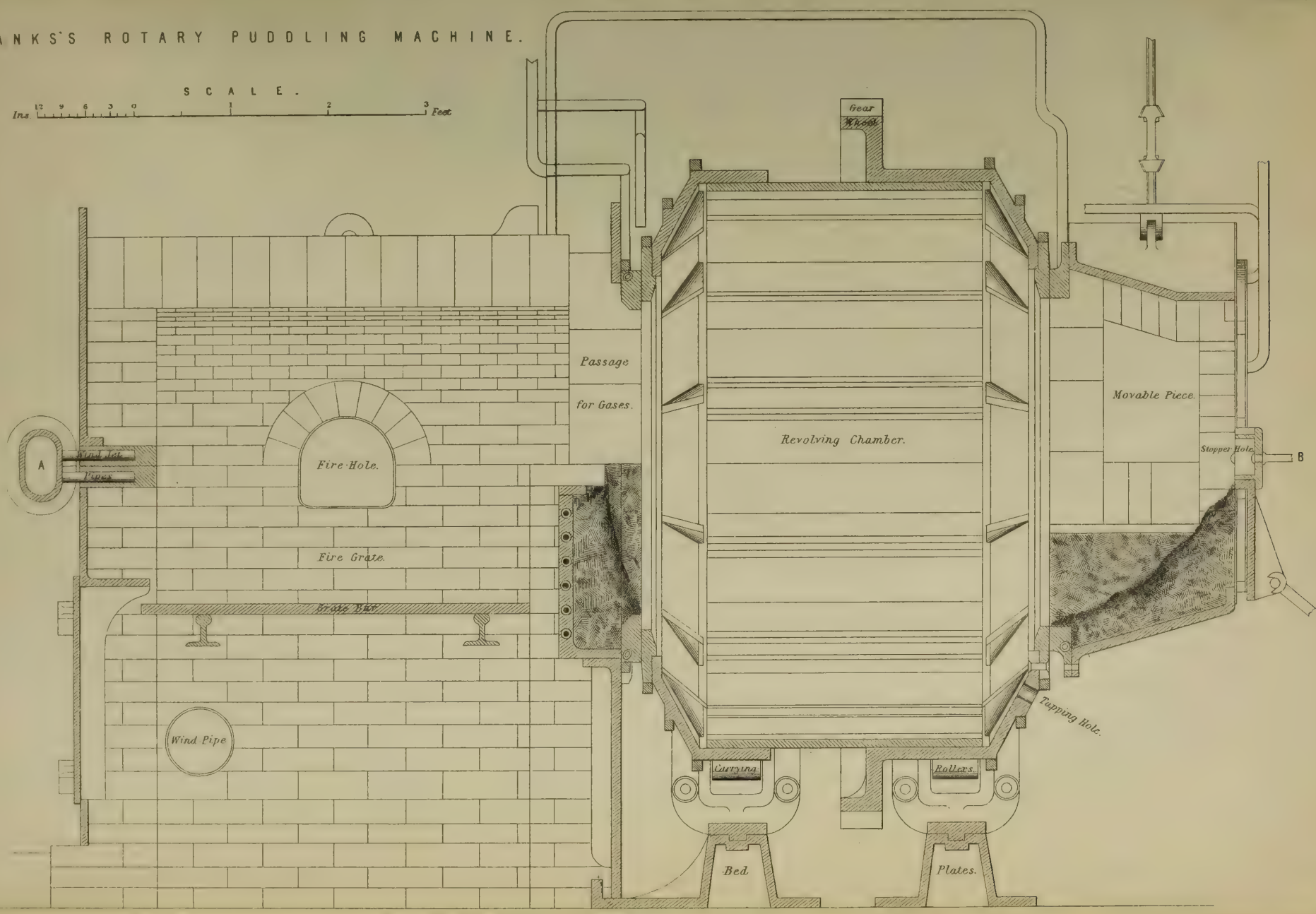
Fig. 27.

the alterations recently suggested by J. Williams of Pittsburg, U.S., who has devoted a great deal of attention to this matter.

Crampton has invented an ingenious and very successful method of burning coal dust, and has devised a mechanical puddling furnace having only a single chamber, the fuel being burnt and the puddling performed in it. The casing is of boiler plate and double, the space between having a current of water flowing through it. By this means the shape of the furnace is kept perfect.

Various mechanical tools, such as oscillating rabbles, &c., have been devised to assist the puddler, but these need not be further alluded to.

DANKS'S ROTARY PUDDLING MACHINE.



The following analyses made by SNELUS during the investigation of the DANKS' furnaces will serve to explain the chemical changes taking place during the process of puddling.

CLEVELAND IRON.

	Pig Iron.	Melted Pig.	Partly Refined.	Further Refined.	Puddled Ball.	Puddled Bar.
Iron,	93·195	95·030	96·460	98·088	98·398	98·129
Carbon,	3·180	2·830	2·800	1·170	*·150	*·150
Silicon,	1·236	·821	·200	·051	·098	·144
Sulphur,	·111	·096	—	—	—	·036
Phosphorus,	1·494	·913	·582	·519	·452	·468
Manganese,	·634	—	—	—	—	·144
Titanic acid,	—	—	—	—	—	·940
	99 850	99·690	100·042	99·828	99·088	100 011

* Under.

SLAGS PRODUCED.

	Tap Cinders.	Slag at end of Process.
Ferrous oxide,	—	56 571
Ferric oxide,	—	6·857
Silica,	21·54	6·730
*Titanic acid,		18 500
Phosphoric acid,	2·353	2·770
Sulphur,	·387	·207
		91·635
Iron,	60 34	48·8

* Ilmenite had been used for fettling the furnace.

STAFFORDSHIRE IRON—METAL.

	Pig Iron.	Melted Pig.	Partly Refined.	Puddled Bar.	Coarse Puddle Bar.	Fine Puddle Bar.
Iron,	93·298	95·680	96·548	95·749	98·430	89·315
Carbon,	2·745	2·550	2·500	—	—	—
Silicon,	2·253	·921	·270	·382	·191	·905
Sulphur,	·130	·113	·072	·050	—	—
Phosphorus,	·632	·358	·295	·246	·215	·396
Manganese,	·914	·432	·180	·158	—	—
Titanic acid,	—	—	·050	1·200	·325	2·520
	99·972	100·054	99·915	97·785	99·161	93·136

SLAGS PRODUCED.

		Tap Cinder.
Ferrous oxide,	68·91	63·900
Ferric oxide,	2·00	3·550
Silica,	12·63	15·750
Titanic acid,	8·75	10·890
Phosphoric acid,	·63	·932
Sulphur,	·33	·355
Alumina, lime, magnesia, &c.,	not estimated.	not estimated.
	—	—

"WHITE PIG," PUDDLED BY HAND.

	Pig Iron.	Puddled Bar.	Puddled Bar.
Iron,	94·471	97·702	—
Carbon,	2·580	under ·150	—
Silicon,	1·568	·545	·424
Sulphur,	·370	·078	·107
Phosphorus,	·896	·430	·518
Manganese,	·115	—	—
	100·000	98·905	—

DERBYSHIRE IRON—METAL.

Iron,	92·510	95·678	97·750	98·071	96·682
Carbon,	3·113	2·900	1·350	* ·150	—
Silicon,	2·151	·466	·170	·221	·387
Sulphur,	·016	·015	—	—	·049
Phosphorus,	1·040	·513	·328	·226	·213
Manganese,	1·008	·144	·028	—	·057
Titanic acid,	—	—	·130	·520	1·110
	99·838	99·716	99·756	99·188	98·498

* Under.

"GREY PIG," USED FOR MAKING TIN PLATE—METAL.

	Pig Iron.	Puddled Bar.	Coarse Puddled Bar.	Fine Puddled Bar.	Wire Fencing.
Iron,	—	98·280	98·696	92·83	98·033
Carbon,	—	—	—	—	—
Silicon,	3·238	·488	·387	1·297	·276
Sulphur,	·108	·019	—	—	—
Phosphorus,	·216	·058	·056	·160	·064
Manganese,	·424	·072	—	—	—
	—	98·917	99·139	94·287	98·373

SLAGS PRODUCED.

	Cinder.	Cinder.
Ferrous oxide,	54·55	52·05
Ferric oxide,	4·30	3·86
Silica,	17 57	11·87
Titanic acid,	12·40	14·80
Sulphur,	·247	·16
Phosphoric acid,	3·971	2·10
	93·038	84·84

SLAGS PRODUCED.

		Tap Cinders.	
Ferrous oxide,	59·14	—	—
Ferric oxide,	20·94	—	—
Alumina,	1·76	—	—
Oxide of manganese,	1·21	—	—
Lime,	·25	—	—
Magnesia,	·42	—	—
Sulphur,	·33	·29	·135
Phosphoric acid,	1·20	1·13	1·678
Silica,	14·17	17·29	19·620
	99·42	—	—
Metallic iron,	—	54·02	53·82

COMMON WELSH "CRYSTALLINE PIG."

	Metal.				Slag	
	Pig Iron.	Melted.	Partly Refined.	Puddled Bar.		Tap Cinder.
Iron,	93·881	97·475	98·831	—	Iron,	52·37
Carbon,	2·310	1·290	—	—	Silica (chiefly),	24·77
Silicon,	·895	·182	·172	·333	Sulphur,	·37
Sulphur,	·763	·251	·070	·064	Phosphoric acid,	3·36
Phosphorus,	2·176	·861	·407	·386		
Manganese,	·115	—	—	·057		
Titanic acid,	—	—	—	—		
	100·140	100·059	99·480	—		—

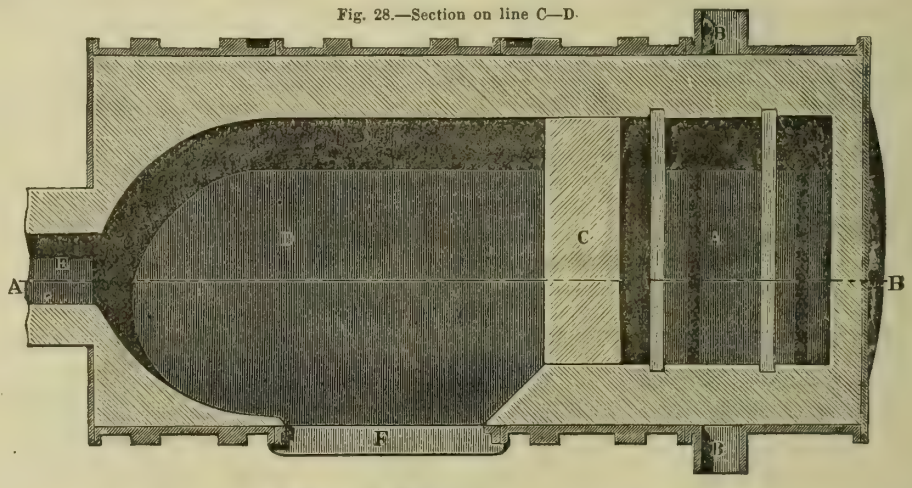
"WHITE PIG IRON" FOR MAKING ORDINARY BARS—METAL.

	Pig Iron.	Puddled Bar.
Iron,	94·850	—
Carbon,	2·512	—
Silicon,	1·091	·312
Sulphur,	·722	·068
Phosphorus,	·567	·230
Manganese,	·201	·028
	99·943	—

Subsequent Treatment of the Puddled Iron. — After the ball of puddled iron is brought from the furnace it is roughly hammered or squeezed into a flat slab, and then rolled out into a bar. The bars are of various widths and thicknesses, according to the purpose for which they are to be subsequently devoted. If the object is to make merchant iron, the bars are usually 5 or 6 inches wide and about three-quarters thick; if for plates, the bars are made from 12 to 16 inches wide and 1½ inch thick. After this first rolling the iron is denominated puddled bar, or muck bar. In this state it has a very rough ragged appearance, and contains a good deal of cinder.

The bars are cut into lengths of 3 or 4 feet, six

Fig. 28.—Section on line C—D.



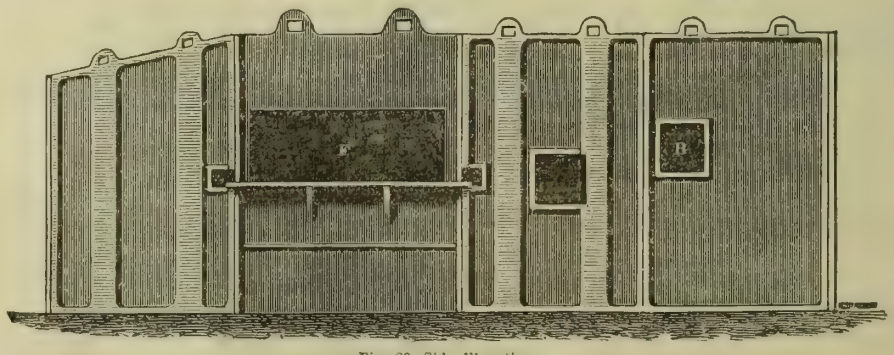
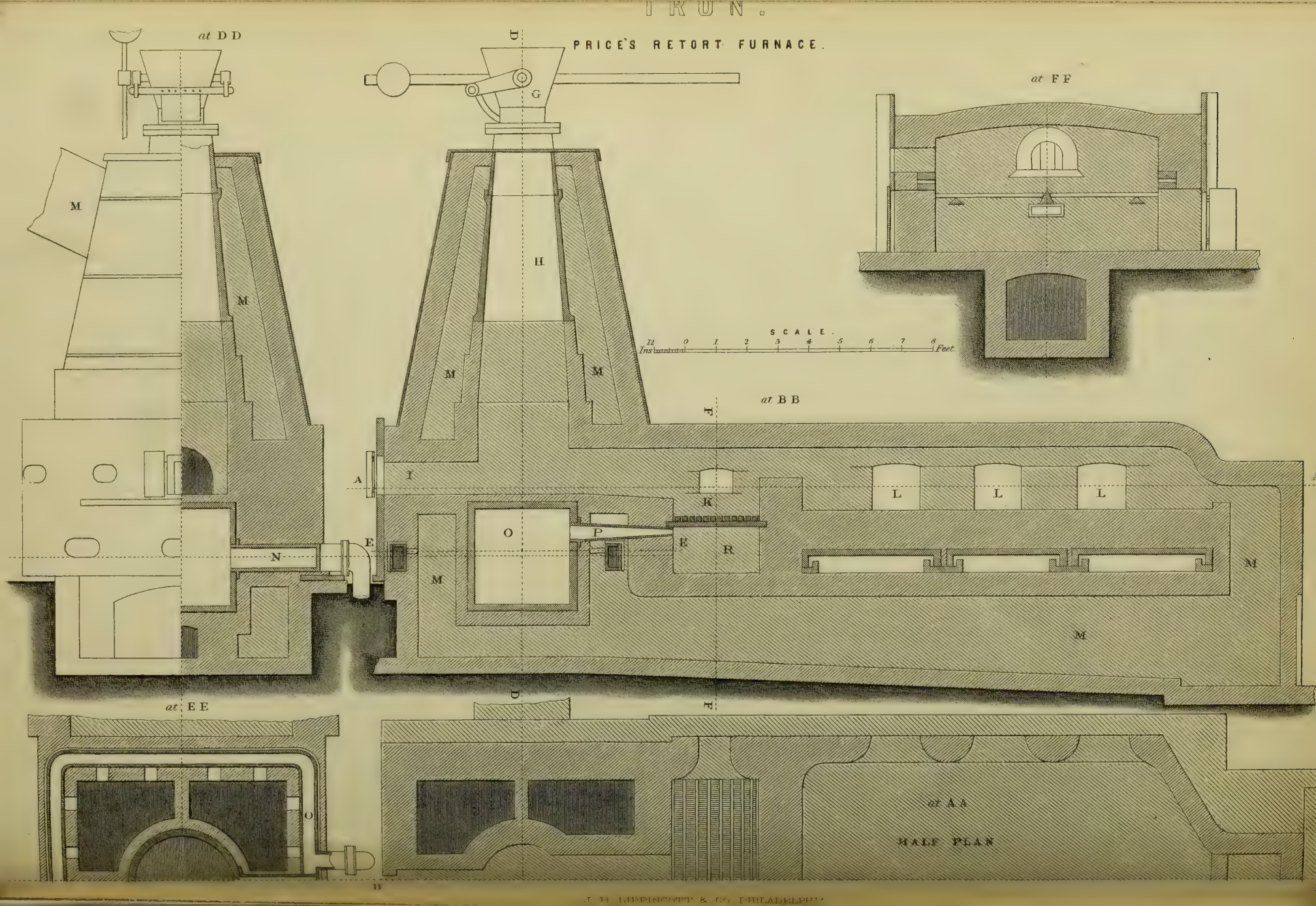


Fig. 29. Side Elevation.

or seven of these piled together, heated, and rolled down into "No. 2" iron, which may be cut up, piled, and rolled into a superior quality of merchant bar. If plates are the object of manufacture, puddled bar slabs are used for the top and bottom of the pile, the shearings from previously rolled plates are placed

IRON.



J. B. LIPPINCOTT & CO. PHILADELPHIA

between them, and the whole heated and rolled into a finished plate. This is the ordinary course of manufacture, and a somewhat similar plan is followed for making iron rails; but in the South Yorkshire district around Bowling and Lowmoor, a much more careful mode of proceeding is adopted. In the celebrated works of this district the puddled iron (which is worked in small charges) is hammered into a slab, which is broken up into small pieces, all of which are carefully examined and selected according to the fracture. The perfectly puddled portions are piled together, heated, and again hammered into a slab, which is rolled down, cut up, piled again, again heated, hammered, and then rolled into a plate. Figs. 28, 29, 30, 31, and 32 will explain the ordinary coal heating furnace for plates. A is the fire place; B, coal charging hole; C, bridge; D, furnace bed; F, charging door; G, ash pit. The gas furnace of SIEMENS' is now much used for heating iron and steel, and is clean and economical in coal. The Ponsard furnace is a modification of SIEMENS', the producer being put close up to the furnace proper. Plate V. illustrates a new form of heating furnace designed by PRICE. In this the fuel itself is heated in the retort, H, by the waste heat which is passed around it before escaping to the chimney. The air is also heated by the same means in passing through the pipes and blast box, O, O. A very high temperature can be obtained by this furnace with a very small consumption of coal. G, coal charging box; I, poking hole; K, fire-grate; L, charging doors; M, waste heat flue and chimney; N, blast pipe inlet; P, blast pipe outlet; R, ash-pit. The waste in these processes is necessarily great, and the manufacturing costs high; but the product is remarkably good. The soft steel recently introduced, which is of excellent and trustworthy quality, capable of standing more severe tests every way than Lowmoor iron, and can be made at a much less cost by either the

Fig. 30.—Side Elevation.

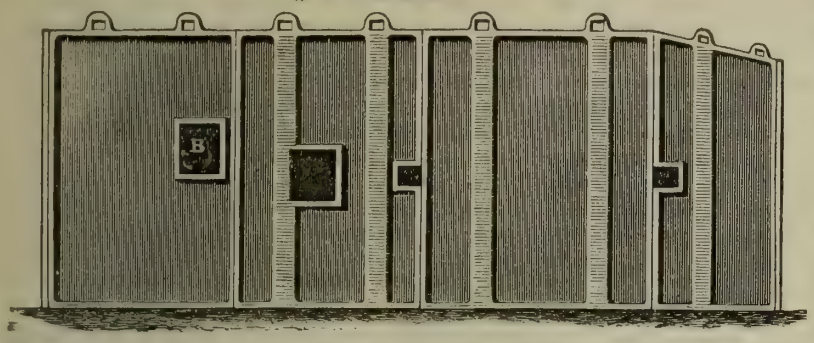


Fig. 31.—Section on line F—E.

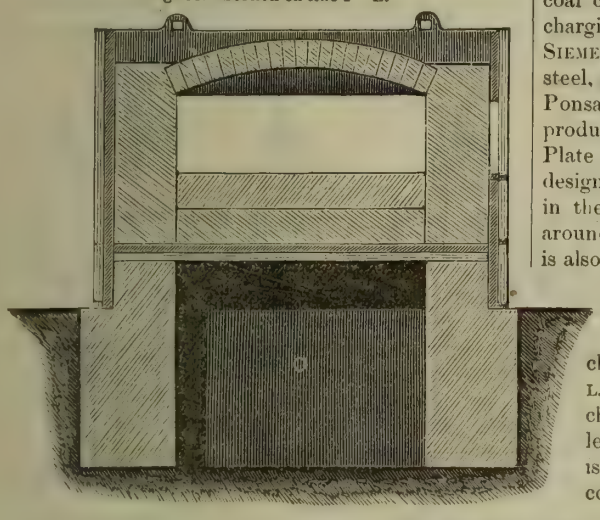
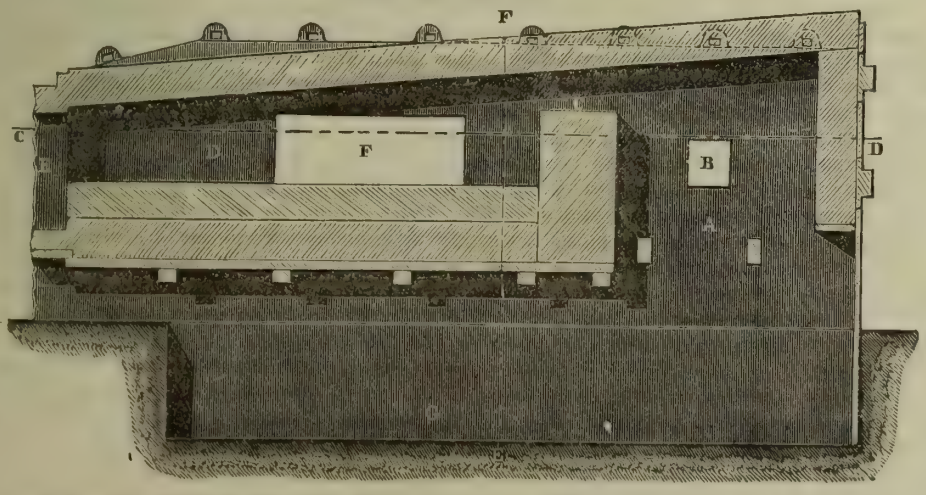
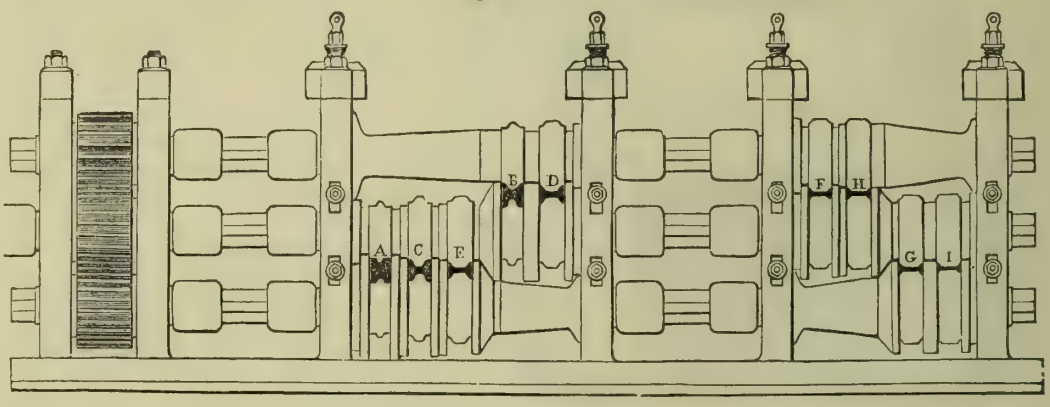


Fig. 32.—Section on line A—B.



Bessemer or the Siemens process, will undoubtedly gradually take the place of these high-class iron plates. Plates are made from piles (varying in weight according to the size required) by heating to a full white heat, and then passing several times through a pair of cylindrical rollers termed the "soft" rolls, by which the different portions are welded together and formed into a rough plate. This is then reheated and passed between a pair of finishing or "hard" rolls, which are kept carefully turned to a true surface. If the piles are not heavy, they are rolled off from the soft rolls without further heating. For light plates the rolls are about 18 to 20 inches diameter and 4 feet long, and the plate after passing through the rolls is returned over the top roll, and so on till it is reduced to the right thickness, the top roll being balanced and screwed down after each pass. For very thin plates, and for tin plates, the rolls are shorter and the plates are doubled and doubled again, so that several are rolled together and opened out after cooling. For plates of 10 cwts. and upwards larger rolls are employed, and they are made to reverse either by a clutch arrangement on the driving shaft, or by reversing the engines after each pass. Rolls 36 inches in diameter and 11 feet long are now being employed. Armour plates are rolled in a similar way, but from much larger piles. Merchant bars are formed by passing the piles between *grooved* rolls, of such a form that the section of the pile is gradually changed to the required form. Rails are rolled in a similar way. For light merchant bars the rolls should run at about 120 revolutions per minute, and for very small sections and for wire still faster. For rails a speed of from 60 to 80 revolutions is generally employed. The plate engraving of a rail mill train (Plate VI.) will show the arrangement employed for this purpose. The pile, which is now generally made sufficiently heavy for two lengths of rails, is heated and cogged or roughed down into a bloom about 8 inches square. This is usually done in a pair, or a set of three grooved rolls. At Dowlais and Ebbw Vale a special arrangement, termed While's blooming mill, is employed for this purpose. This consists of a set of two pair of horizontal, and

Fig. 33.

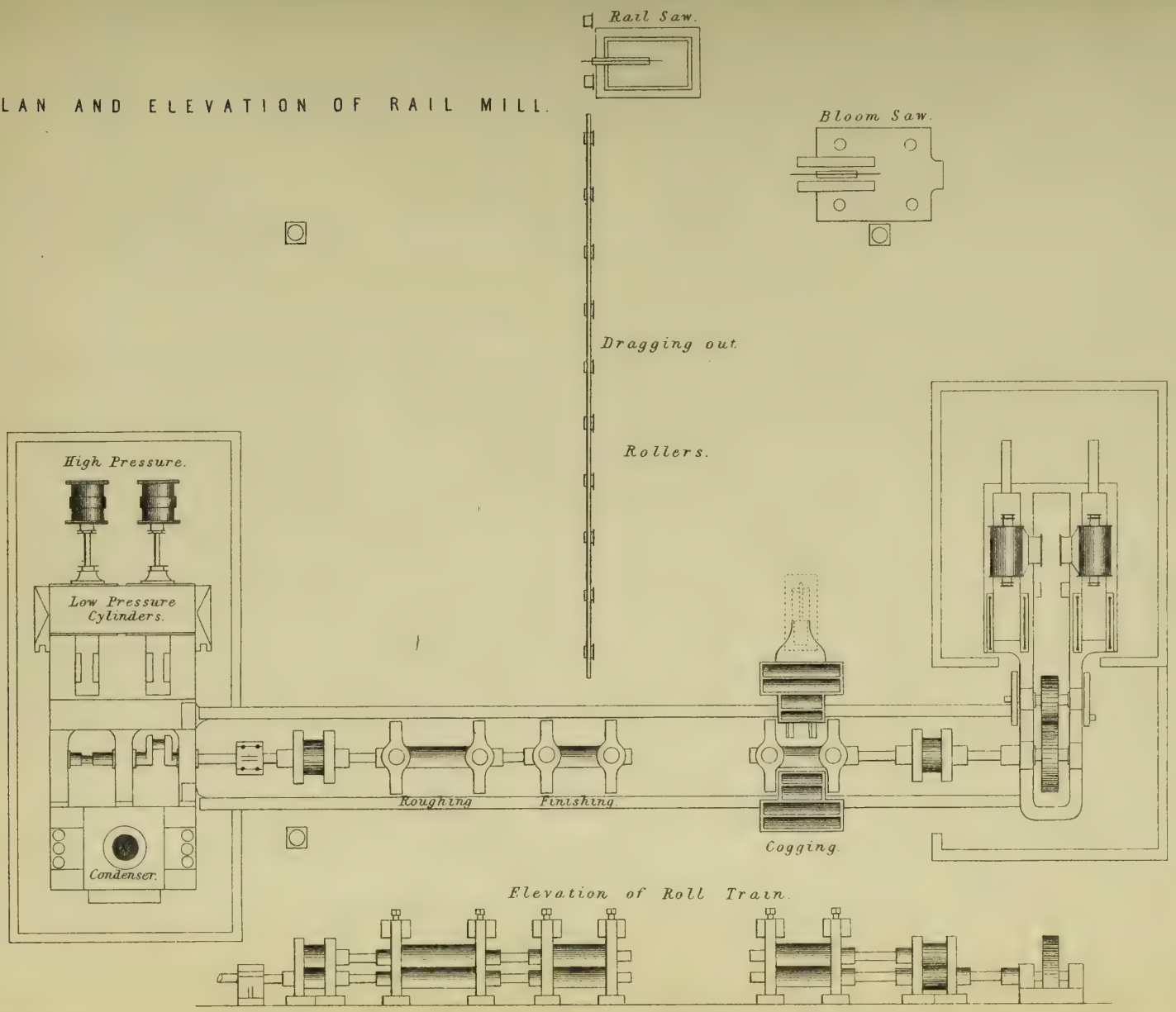


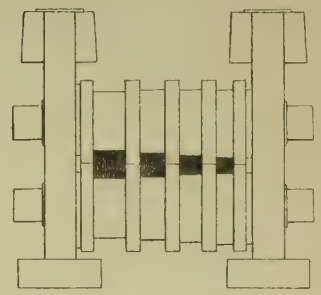
one pair of vertical grooved rolls running between them, so arranged that by one pass of the pile it gets squeezed on all sides. This avoids the necessity for turning over the pile, an operation which is requisite when blooming in ordinary rolls. After cogging the bloom is reheated, or "wash" heated, and passed first through a set of "roughing" rolls and finally through the "finishing" train. Great skill is required on the part of the roll turner to arrange the draught of the rolls, so that the work done at each pass may be as equal as possible, and that a perfect section may be obtained at finish. For light rails, as for plates, a "pull over" mill is employed, but for heavy rails a reversing mill or three-high rolls are necessary to save time and the labour of passing the bar over the top roll. In all cases it is necessary to place side guards on a framing in front of the rolls to lead the piece into the grove, and guides to prevent the piece coiling around the roll when passing through. Where three-high rolls are used the top guides are hung from a frame and balanced. A. Thomas, of Clabecq, Belgium, has lately devised a plan of three-high rolls by which a considerable saving in weight is effected, as is shown in Figs. 33, 34, 35, 36, 37, 38, 39, and 40. The first housing holds the pinions, the second the roughing rolls, and the third the finishing rolls. Accompanying are five other dispositions of trains.

Figs. 33, 34, 35, 39, and 40 are various modes of construction of these mills; Fig. 36 that of a two-high mill; Figs. 37 and 38, of the ordinary three-high mills in common use.

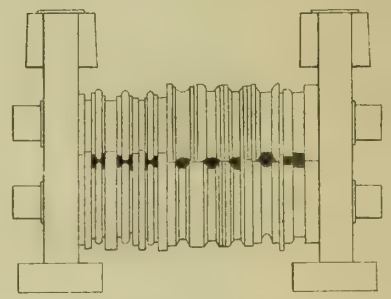
These five modes of establishing rolls are all for the same number of grooves of equivalent sizes. It may be remarked that the length of table of Fig. 36, the two-high mill, is 1·70 mètre for a diameter of 0·600 mètre. The new trains, Figs. 35, 39, and 40, have exactly the same width and the rolls the same diameter; whereas in the ordinary three-high, Fig. 37, for the same number of grooves, the table has to be 2·110 mètres in breadth, and the diameter of rolls increased in consequence to 0·644 mètre, so as to obtain the same amount of resistance. In order to have the same number of grooves on the three-high, Fig. 38, as on Figs. 35, 39, and 40, the table must be 2·043 mètres, and the rolls have a diameter of 0·637 métre

PLAN AND ELEVATION OF RAIL MILL.

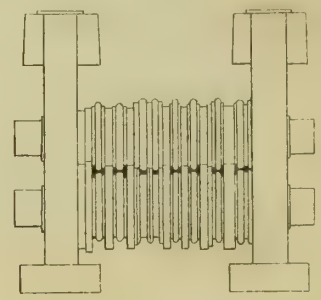




Cogging Rolls.



Roughing Rolls



Finishing Rolls

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		Kilos.
Total weight of ordinary three-high mill,	Fig. 37, is	14,244
"	Fig. 38, is	13,193
" new "	Fig. 35, is	9,479
" "	Fig. 39, is	8,522
" ordinary two-high mill,	Fig. 36, is	7,541
" new three-high mill,	Fig. 40, is	7,477

As will be noticed, the last combination of three-high rolls weighs less than the corresponding ordinary two-high.

Lauth has also modified the three-high plate mill by making the middle roll smaller than the others, and allowing it to run free. Fig. 41 shows the

Fig. 34.

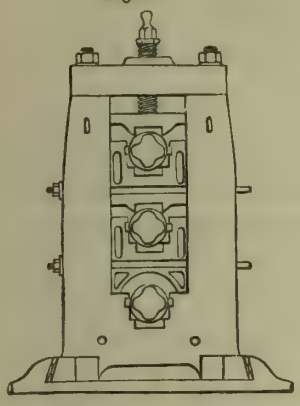


Fig. 35.

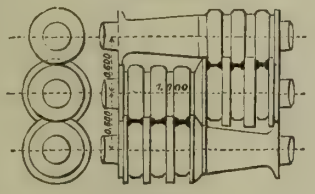


Fig. 36.

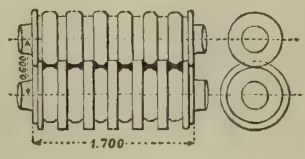


Fig. 37.

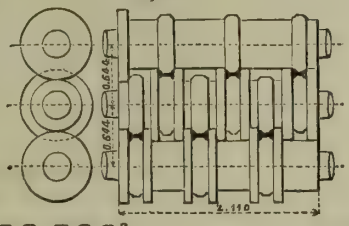
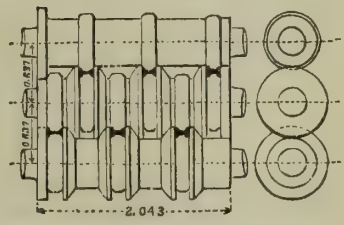


Fig. 38



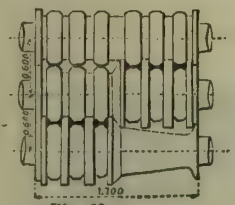


Fig. 39.

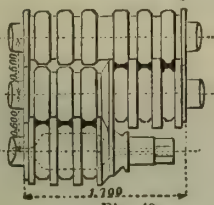


Fig. 40.

arrangement of rolls in Brown's mill; the piece passes through a hole in the first pair, and out freely through an open groove in the second pair.

Menelaus also uses four rolls; Fig. 42 shows the arrangement.

P. Kirk of Workington has recently introduced a five roll system for roughing, shown in Fig. 43.

By this plan the piece is squeezed twice at one pass, and once on the return.

One of the most effective arrangements for rail rolling is that designed by Holland. He uses a three-high mill for roughing, and a two-high reversing mill for finishing, placing the two close together, so that the rail has but little distance to pass over in changing from one to the other.

Angles and girders are rolled in a similar way as rails.

After the rails have been rolled they are cut to

Fig. 41.

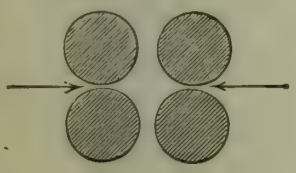


Fig. 42.

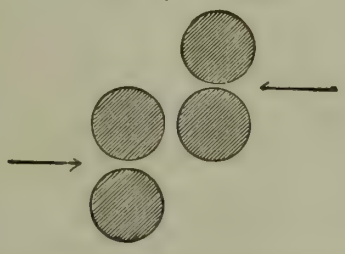
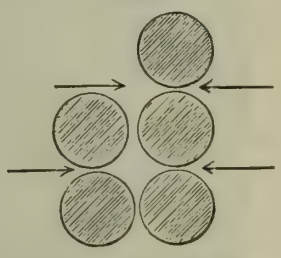


Fig. 43.



length, while hot, by a circular saw revolving about 1000 times per minute. When cold they are straightened by a series of impacts from a reciprocating press, success depending entirely upon the eye and skill of the man in charge.

The enormous development of railways has led to a corresponding increase in rolling mills, and the production of rails has now become one of the most important manufactures in the country. The great improvements that have taken place in the manufacture of steel have, however, so cheapened its cost that steel rails can now be sold for little more than iron; and as they are far more durable, the iron rail has almost entirely given place to steel. Doubtless, before many years are past, the same will have to be said with regard to plates. At present only the purest ores can be used for making pig iron that is designed for conversion into steel; but all the energy of the trade is being devoted to free the poorer ore from its phosphorus, or to remove this deleterious element in some of the subsequent processes; and whenever this is accomplished, the manufacture of steel will receive a great impetus. Cleveland pig iron would be perfectly suitable for conversion into steel were it not for the phosphorus; and it is confidently believed that its expulsion from the iron as

easily as carbon and silicon will before long be an accomplished fact.

Statistics of the Iron Manufacture.—The Hon. A. S. HEWITT, of New York, gives the following estimate of the world's production of iron. The figures for Great Britain and France are for 1874, Austria and Hungary, 1873, other countries, 1872 or 1871.

Great Britain,	5,991,000
United States,	2,401,000
Germany,	1,600,000
France,	1,360,000
Belgium,	570,000
Austria and Hungary,	365,000
Russia,	360,000
Sweden and Norway,	306,000
Italy,	73,000
Spain,	73,000
Switzerland,	7,000
Canada,	20,000
South America,	50,000
Japan,	9,000
Asia,	40,000
Africa,	25,000
Australia,	10,000
	13,260,000

The make of pig iron in two of the most important centres of the United Kingdom has been—

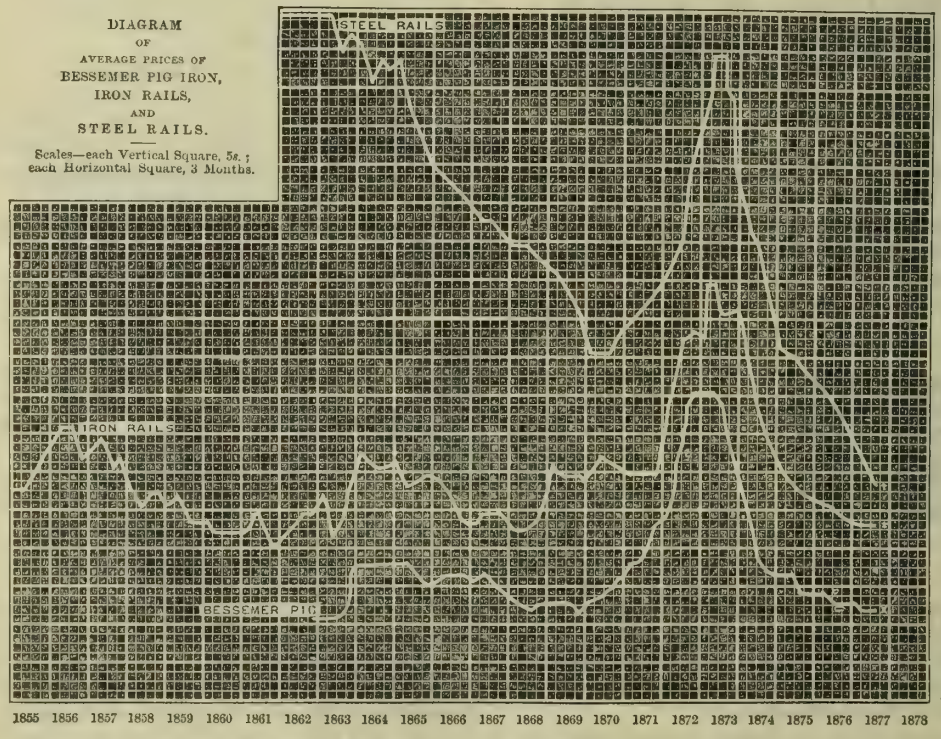
	Cleveland. Tons.		Scotland. Tons.
1868,	1,233,418	....	1,068,000
1869,	1,459,508	....	1,150,000
1870,	1,695,377	....	1,206,000
1871,	1,884,239	....	1,160,000
1872,	1,968,972	....	1,090,000
1873,	1,999,491	....	993,000
1874,	2,001,233	....	806,000
1875,	2,047,763	....	1,050,000
1876,	2,075,565	....	1,103,000

The exports from the United Kingdom have been in tons—

	1873.	1874.	1875.	1876.
Pig iron,	1,142,065	776,116	947,827	905,029
Bar, angle, bolt, and rod iron,	286,845	258,953	276,068	227,714
Railroad iron of all sorts,	758,014	782,665	545,981	413,656
Iron or steel wire	29,445	36,692	43,221	44,959
Hoops, sheets, boiler and armour plate,	201,570	168,430	204,483	192,387
Tin plates,	120,638	122,960	138,363	132,397
Unenumerated cast and wrought iron,	282,000	257,069	239,869	243,482

Fig. 41 is a diagram showing the changes that have taken place in the price of steel and iron over a period of years.

Fig. 44.



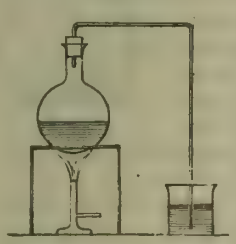
Average price of Steel Rails, £18 10s. per ton for first three years.
Average price of Steel Rails, £13 per ton for last ten years.
Average price of Iron Rails, £7 10s. per ton for last ten years.
Average price of Iron Rails, £6 10s. per ton, ten years ending 1864.
Average price of No 1 Bessemer Pig, £4 15s. 1d. per ton, for last ten years.

Method for Complete Analysis of Iron Ores.—After the ore has been sampled and pounded so as to pass through No. 40 sieve, determine the percentage of moisture (hygroscopic water), as follows:—About 5 grams. of the ore are to be dried in a water oven heated to 100° C., until, on weighing, it ceases to lose weight. The loss in weight is moisture.

Determination of Iron.—About 1 gram. of the ore,

after being well dried at 100° C, and finely pulverized, is digested in a small flask with hydrochloric acid, a funnel being inserted in the neck of the flask to prevent any of the solution escaping. After digesting for about twenty minutes, the residue by that time will generally be found white (unless there is organic matter present in the ore). The solution is diluted to about half a pint, and the iron is reduced by adding metallic zinc, or by adding a solution of protochloride of tin, until on testing a drop of iron solution with a drop of sulphocyanide of potassium on a porcelain slab, it ceases to give a blood-red coloration. When the iron is thoroughly reduced, the solution will be colourless. When this is accomplished proceed to estimate the iron by following process:—A solution of bichromate of potash is made of strength that 1 c.c. equals about ·01 per cent. of iron; 42 grams. of bichromate of potash dissolved in 2 litres of water give the desired strength. The solution is to be standardized with iron or steel of a known composition. Transfer the iron solution to a porcelain dish, care beng taken to well wash the flask, and to add the washings to the rest of the solution in the basin. The bichromate solution is then gradually run in from the burette, and the mixture repeatedly stirred and tested by taking a drop of iron solution, and mixing with a drop of ferricyanide of potassium (of strength about 1 part of salt to 45 of water). When the solution ceases to give a blue coloration when tested on a white slab, the divisions used should be noted, and multiplied by strength of bichromate solution. To estimate the quantity of ferrous oxide in the ore, take about ·5 gram. of ore, digest in a test tube with hydrochloric acid, and test a drop of solution with ferricyanide of potassium. Should there be a dark blue coloration, protoxide of iron is present. If it is required to estimate the relative quantities of ferric and ferrous oxides, as in the case of a complete analysis of a magnetic ore, two estimations must be made—one as already described, and the other as follows:—

Fig. 45.



About 1 gram. is to be digested with hydrochloric acid for 20 minutes; but instead of a small funnel in neck of flask, a tight fitting cork with a small glass tube must be inserted, and the tube led into a beaker of water. No further description is necessary, as it must be obvious that the above arrangement is to exclude the air in order to prevent the FeO becoming oxidised to Fe_2O_3. Fig. 45 will explain the arrangement.

As soon as the iron is dissolved take away the lamp, and the water in the beaker will rush into the flask, and thus dilute the solution ready for estimating with bichromate. The water used for washing the flask must have been previously boiled, as well as the water in beaker, in order to expel the air.

Determination of Bases.—From 1 to 2 grams. of ore finely pulverized is digested in a mixture of nitric and hydrochloric acid, and evaporated to dryness. Redissolve in hydrochloric acid, dilute with water, and filter. Wash filter with a weak solution of hydrochloric acid, and ultimately with water. Filter contains insoluble residue. Ignite and weigh. The residue generally consists for the most part of silica and clay, but often contains iron, alumina, lime, magnesia, &c.

If it is necessary to examine the residue further, it must be fused in a platinum crucible with mixed carbonate of potash and soda, dissolved in water, decomposed with hydrochloric acid, and evaporated. Digest with hydrochloric acid, then dilute and filter. The residue is silica, which must be well washed, ignited, and weighed. The Al_2O_3, CaO, MgO, Fe_2O_3, &c., are separated as follows:—To the above filtrate, or to the filtrate from the insoluble residue, add bromine in order to precipitate manganese (this will be more fully described further on), then ammonia; boil, and filter. Precipitates contain iron, alumina, manganese, and phosphoric acid. Dissolve in least quantity of hydrochloric acid, and boil in a platinum dish with excess of caustic potash; by this means the alumina along with the phosphoric acid is dissolved. Dilute, and filter. To the filtrate add hydrochloric acid till acid, and then add ammonia. Filter, wash well, and weigh precipitate as alumina, deducting percentage of phosphoric acid, as determined by a separate estimation. (For estimation of manganese see further on.) To the first ammoniacal solution add oxalate of ammonia, boil, filter through Swedish filtering paper, ignite, and then add a few drops of sulphuric acid in order to convert carbonate of lime into sulphate; ignite again, and weigh as such. Evaporate filtrate from lime to small bulk in a beaker, and precipitate magnesia with phosphate of soda. Allow to stand for twenty-four hours. Filter, and wash with slightly ammoniacal water. Ignite, and weigh precipitate as pyrophosphate of magnesia.

Determination of Manganese.—The following description by Riley embodies the results of his recent investigations:—

For the determination of manganese in manganiferous iron ores, I would suggest that about 1 gram. or 15 grains of the ore dried at 212° Fahr. should be dissolved in hydrochloric acid, the siliceous matter separated by filtration, and the larger portion of the free hydrochloric acid driven off from the acid portion of the filtrate, reserving the washings to make the bulk of the liquid up to about one-third of a litre or half a pint; the solution should be allowed to stand four hours, to see if any baryta separates after adding previously a few drops of sulphuric acid.

If any sulphate of barium separates it must be filtered off; if not, the analysis may be proceeded with. The solution should be diluted to about 1 quart or 1 litre, made neutral, or until the solution is slightly turbid with ammonia, and acetate of ammonia added; the solution then boiled, after boiling allowed to settle and filtered.

After filtration, and without washing, the precipi-

tate is redissolved in hydrochloric acid, and again precipitated with ammonia and acetate of ammonia. The basic ferric acetate, after settling, is filtered off and washed 3 or 4 times with boiling distilled water, adding each time a few drops of acetate of ammonia to prevent the oxide of iron passing into the filtrate, and to facilitate the filtration. The filtrate must be reduced by evaporation to $1\frac{1}{2}$ litre or 3 pints, and when cold bromine is added (2 to 4 cubic centimètres). The solution is well agitated in the flask by shaking until it is saturated with bromine, leaving only a little at the bottom undissolved; ·880 ammonia is now added in excess, shaking violently the flask; the liquid is then gradually warmed up to the boiling point for about an hour, then boiled a few minutes, the hydrated binoxide of manganese allowed to settle, then filtered off, and the precipitate dried. The filter first incinerated thoroughly, the binoxide of manganese added, heated with the lid on for a few minutes until red hot, then ignited from a quarter of an hour to twenty minutes over a Bunsen burner, or better, in a muffle; if only over a Bunsen burner it should afterwards be ignited over a gas blow-pipe to see that it does not lose weight. A platinum crucible should be used, unless the ignition is made in a muffle.

The tri-mangano-tetroxide of manganese (Mn_3O_4) should then be dissolved in a small quantity of hydrochloric acid. If there is any insoluble residue, which occasionally occurs, it should be filtered off, a drop or two of sulphuric acid added to see if baryta is present; if any precipitate occurs, it must be separated. To the filtrate or solution is added acetate of ammonia in excess, and sulphuretted hydrogen is passed through it to saturation.

The precipitate (a small amount is universally obtained) is filtered off and weighed. Should this weigh more than ·05 of a grain, or 3 milligrams., the excess over and above this should be deducted from the oxide of manganese weighed.

I think this small amount should be allowed, as the precipitate occasionally contains traces of manganese, and the filtrate from the precipitation of the manganese by bromine and ammonia also contains a faint trace of manganese. This filtrate, in all cases, should be evaporated down to about half a litre, or nearly a pint, and tested with bromine and ammonia, to see if all the manganese is separated. As a rule, either none is obtained or a mere trace.

Determination of Sulphur.—About 5 grams. of the ore are digested with mixed nitric and hydrochloric acids, and evaporated to dryness. It is important to test both hydrochloric and nitric acids for sulphur compounds by a blank analysis (acids that are sold as pure are often found to contain sufficient sulphur compounds to invalidate the result); redissolve in hydrochloric acid, and filter. To filtrate add chloride of barium; boil for about an hour, then allow to settle and filter through Swedish filtering paper; ignite precipitate, and weigh as sulphate of barium.

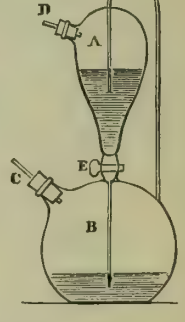
Determination of Phosphoric Acid.—If the percentage of phosphoric acid is approximately known, it is advisable to take as much ore as will make the yellow precipitate weigh not more than ·5 gram. If more is suspected, take 1 gram. of the ore. In the case of a pure ore, such as Cumberland hema'ite, 5 grams. should be taken and digested in mixed nitric and hydrochloric acid; evaporate to dryness, redissolve in hydrochloric acid, and filter. To the filtrate add ammonia until alkaline, and redissolve in slight excess of nitric acid, and boil. Then add an ammoniacal solution of molybdate of ammonia more or less, according to quantity of precipitate. Great care should be taken that molybdic acid is not mistaken for phospho-molybdate of ammonia. The proper precipitate is fine and granular, and can easily be distinguished from molybdic acid, which is more flocculent. After the addition of molybdate solution the flask is to be well shaken, and then allowed to settle in a warm place. Filter and wash with water containing 1 per cent. of nitric acid. Test filtrate with more molybdate solution and shake well, and allow to settle, to see if all phosphoric acid has been precipitated. Dry precipitate in water bath at 100° C. When dry, detach from filter paper and weigh. Composition of precipitate is as follows:—

Molybdic acid,	91·69
Phosphoric acid,	3·72
Ammonia,	3·41
Water,	1·18
	100·00

Determination of Carbonic Acid.—The usual method adopted in this estimation is by noting the loss on a weighed quantity of ore after the addition of sulphuric acid, which evolves the carbonic acid.

Fig. 46 shows a convenient apparatus for this estimation: A contains sulphuric acid; B contains water; E is a glass tap; C is stopped with a piece of india-rubber tubing, containing a glass rod. Take about 1 gram. of ore in B with the fresh water, and weigh the apparatus. Then allow about half of the sulphuric acid to enter B. Put on a warm plate until no more carbonic acid is given off, then remove the stopper at C, and attach an india-rubber tube to D, and draw air through C, in order to expel the remaining carbonic acid in apparatus. Allow to cool and weigh. The loss is carbonic acid.

Fig. 46.



Determination of Combined Water.—About 1 gram. of ore dried at 100° C. is put into a bulb of hard glass, attached to which is a tube filled with chloride of calcium. On weighing the calcium tube before igniting ore and after, the increase of weight gives the combined water.

Determination of Alkalies.—Mix 1 part of the finely pulverized mineral, 5 to 6 of carbonate of calcium, and one-half to three-fourths of chloride of ammonium; introduce the mixture into a platinum crucible, and heat to bright redness from thirty to forty minutes.

The mass as it comes from the crucible is placed in a capsule with water, and then heated in a sand bath for two or three hours, renewing the water from time to time as it evaporates. The contents of the capsule are next thrown on a filter, and the water passes through, containing the chloride of the alkalies, a little chloride of calcium, and caustic lime; all else that the mineral may have contained remains on the filter, except baryta and strontia.

To the filtrate add carbonate of ammonium, and boil for some time, when all the calcium will be precipitated as carbonate; add a few drops of a solution of carbonate of ammonium to the hot solution, to be sure that all the calcium is precipitated. Should this be the case, filter; the filtrate will contain the chloride of the alkalies and chloride of ammonium; it is evaporated to dryness over a water bath in a small platinum capsule. The capsule is carefully heated to expel the sal-ammoniac, and finally heated to about 400°; it is then weighed with its contents, and the chlorides, if mixed, separated in any convenient way. It is generally found that a small amount of the alkali remains behind, amounting to from two-tenths to 1 per cent. of the mineral used. To obviate this error it is accomplished in the following manner:—After the fused mass has been treated with water, filtered, and washed as above, the filter and its contents are dried; the latter are detached from the filter and rubbed up in a glazed mortar with an amount of sal-ammoniac equal to half the weight of the mineral, and reheated in a platinum crucible, exactly as in the first instance, treated with water, thrown on a filter and washed, the filtrate added to that from the first fusion, the whole treated with carbonate of ammonium, and completed as above described. This method will not answer when boracic acid is present. Copper and zinc, with several other elements, are occasionally present, but the method for estimating these scarcely belong to the present article.

Salts of Iron.—It has already been shown that iron is susceptible of three definite degrees of oxidation, forming monoxide, *i.e.*, ferrous oxide, FeO; magnetic iron oxide, *i.e.*, ferroso-ferric oxide, Fe_3O_4; and sesquioxide, *i.e.*, ferric oxide, Fe_2O_3.

Ferrous oxide dissolves readily in acids, forming ferrous salts. These are mostly soluble and crystallizable. They have a white colour, tinged with blue or green, when dry, and are commonly pale blue or green when hydrated. When exposed to the air they greedily absorb oxygen, and are converted into ferric oxide and ferric salts. Solutions of ferrous salts are blue or blue-green in colour, have an inky taste, and are readily oxidised.

Fixed caustic alkalies precipitate white ferrous hydrate from ferrous solutions. Ammonia precipitates part of the iron only. Alkaline carbonates precipitate white ferrous carbonate. Oxalic acid colours ferrous salts yellow, and ultimately precipitates yellow ferrous oxalate. Ferro-cyanide of potassium gives a white precipitate, ferri-cyanide a deep blue one.

Ferrous Sulphate.—*Green vitriol, copperas; couperose verte*, French; *Eisenvitriol, Schwefelsaures eisenoxyd.*—This salt is obtained pure by dissolving iron filings or turnings in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. The crystals are sea-green transparent rhomboidal prisms. Exposed to dry air, they effloresce; in moist air, the salt gradually absorbs oxygen, and is partly converted into a basic ferric sulphate and ferric oxide, becoming of a rusty or reddish colour, whence the French term *couperose*, corrupted into the English name *copperas*. Bonsdorff has shown that when perfectly pure it does not change vegetable blues, though generally stated to do so, the reddening effect being only produced when some of the iron of the monoxide passes into a higher state of oxidation. It is soluble in 2 parts of cold, and in three-fourths of its weight of boiling water. Crystallized ferrous sulphate contains seven equivalents of water, and is therefore represented by the formula, $FeSO_4.7H_2O$. When heated, it fuses in its water of crystallization, and gives off six equivalents of water at 114° C., but retains one equivalent till heated above 280° C. At a red heat it evolves sulphuric anhydride, and by this process sulphuric acid used formerly to be prepared; hence it was termed *oil of vitriol*. The residue, consisting of ferric oxide, which remained in the vessel, was known under the name of *Caput mortuum vitrioli*, or *colcothar*. The fuming sulphuric acid is still prepared from the sulphate in this manner.

The copperas of commerce is usually prepared from the pyritous schists of the coal measures, in connection with the manufacture of alum. By referring to the article on that subject, it will be seen that iron pyrites (FeS_2) is present in very large proportion in many aluminous schists, and that it is quite as indispensable to the production of alum as the alumina itself. When the schists are subjected to calcination in heaps, the sulphur of the iron disulphide absorbs oxygen from the air, by which it is converted into sulphuric acid, and this combines with the other ingredients, forming an aluminium sulphate and ferrous sulphate. These salts are extracted by lixiviation in the same waters; and therefore the next operation is to separate the iron salt from the aluminous, when both have been obtained in solution in the same vat. For this purpose the solution is evaporated in large cisterns, by carrying the flue of a furnace over its surface, and when sufficiently concentrated is run into coolers, where the sulphate of iron crystallizes, and the aluminium sulphate, being the much more soluble salt, remains in the mother-liquors. (See Alum.)

The commercial article, prepared as above described, generally contains a small proportion of alum, of ferric sulphate, and other ingredients, some of which increase its value for particular purposes. In dyeing black, for example, that copperas is preferred which contains ferric sulphate, and is known by its darker green colour. The excess of acid in some kinds of copperas is objected to; and those in which the crystals are small do not fetch so high a price as when the crystals are large.

At Paris and Honfleur the materials employed are iron turnings and shavings, and sulphuric acid of 18° or 23° Twaddell, which is also a residue obtained from the rectification of certain lamp-oils. The acid is poured into rectangular copper vessels, strengthened by iron plates, and heated by means of a fire below, the flames of which play under and around the sides of the vessels. The iron turnings, previously sifted, are then introduced, agitating from time to time with wooden stirrers, and adding more turnings in proportion as they dissolve in the liquid. The liquor is maintained for eighteen to twenty hours in a state of constant ebullition, by which it is gradually more and more concentrated. The boiler is covered with a hood, from which the gases and vapours are conveyed through a wide tube into a tall chimney creating a powerful draught.

When the concentration has reached its proper limit, which is known by observing the crystallization when some drops of the solution are put upon a plate of porcelain or earthenware, the liquid is drawn out with a copper pump, and flows by a gutter into a cellar, where it is left for eighteen to twenty-four hours, to deposit the matters in suspension. The clear solution is then transferred by means of a siphon into sluices, by which it is conducted into other vats, measuring about 7 feet in diameter by 3 or 4 in depth.

These are the crystallizing vats. Planks are laid across them, pierced with holes, through which slips of wood are suspended vertically in the solution. The crystals which form on the sticks and on the sides of the vat are transparent, and exhibit the ordinary green colour. At the end of eight or ten days, if the temperature of the air be not too high, the crystallization is finished; and the mother-water is made to flow out, to be conveyed back to the boiler along with the sulphuric acid and iron turnings. The sticks are taken out, and the crystals at the bottom, mixed with impurities, are taken to be redissolved. The crystals adhering to the sticks and to the sides of the vat are detached and rapidly dried, to avoid the formation of a rust-coloured salt, which would tarnish the crystals. They are then put into barrels for the market.

Copperas is extensively used in dyeing black, especially for hats; in making ink and prussian blue; for reducing indigo in the blue vat; in calico-printing; and in many chemical and medicinal preparations. Its value as an ingredient in dyeing black, and in making ink, arises from the special reaction of the iron with the tannin contained in nut-galls, oak-bark, catechu, and different tinctorial substances. It promotes the solution of the indigo by a deoxidation of the colouring principle. On these applications, see the articles DYEING and INK.

Ferric salts are produced by the solution of ferric oxide in acids, or by double decomposition. They are mostly white when anhydrous, yellow or orange-red when hydrated. The chloride is brown-red, the acetate crimson-red, the nitrate nearly colourless. Most ferric salts are soluble in water, and are difficult to obtain in the crystalline state. They are reduced by sulphuretted hydrogen with precipitation of sulphur from neutral or acid solutions. Ammonium sulphide precipitates black sulphide of iron. Alkalies and alkaline carbonates throw down ferric hydrate, insoluble in excess. Potassium ferro-cyanide precipitates prussian blue. Potassium ferri-cyanide forms no precipitate, but turns the liquid brown. Potassium sulpho-cyanate strikes a blood-red colour with solutions of ferric salts.

FERRIC SULPHATE.—*Sesquisulphate of Iron.*—This salt ($Fe_2(SO_4)_3$) is formed by mixing with a solution of ferrous sulphate exactly half as much sulphuric acid as that salt contains, and adding to the mixture in a boiling state successive portions of nitric acid until nitrous fumes cease to appear. The solution is then evaporated to dryness to expel the excess of nitric acid, and the ferric sulphate remains as a white salt. It is formed in the mother-waters of the monosulphate, and, according to DUMAS, the two salts are capable of crystallizing together and forming a kind of double salt. It is this combination which imparts to much of the sulphate of commerce a dingy grass-green colour, whereas the pure sulphate of ferrous oxide furnishes hydrated crystals which are of a bright bluish-green.

Ferric sulphate is also formed by heating brown hematite with strong oil of vitriol, and expelling the excess of acid by heat. HART states that the anhydrous salt is formed when ferrous sulphate is added to boiling concentrated sulphuric acid, and separates on cooling in minute crystalline scales.

Solution of ferric sulphate is of a fine red colour; evaporated it deposits a light yellow paste, which is the hydrate, with a small quantity of acid. This deposit dissolves readily in water. Continuing to heat the acid and water are expelled, and the remaining anhydrous salt becomes much more difficultly soluble. At a red heat it is decomposed into ferric oxide and sulphuric acid.

Iron Cyanides.—Ferrous cyanide is formed when cyanide of potassium is added to a solution of a ferrous salt. Excess of the potassium salt or dilute potash solution converts the precipitate into ferrocyanide, thus—

Ferrous Cyanide.		Potassium Hydrate.		Potassium Ferrocyanide.		Ferrous Hydrate.
$3FeCy$	+	$2KHO$	=	K_2FeCy_3	+	$2FeHO$.

Ferric cyanide, Fe_2Cy_3, has never been isolated. On mixing ferricyanide of potassium with ferric chloride, a dark brown liquid is produced, which probably contains ferric cyanide.

Potassium Ferricyanide.		Ferric Chloride.		Potassium Chloride.		Ferric Cyanide.
$K_4Fe_2Cy_6$	+	Fe_2Cl_3	=	$3KCl$	+	$2Fe_2Cy_3$.

On evaporating this solution, chlorine or cyanogen is given off as either reagent is in excess, and prussian blue is produced.

Ferrocyanides are combinations of ferrous cyanide with other metallic cyanides; they have the constitution, $(MCy)_4Fe_2Cy_2 = M_4Fe_2Cy_6$.

Ferricyanides, in like manner, are compounds of ferric cyanide with other cyanides, $(MCy)_3Fe_2Cy_3 = M_3Fe_2Cy_6$. (See POTASSIUM.)

STEEL is treated of in a separate article, *q.v.*

LEAD.—French, *Plomb;* German, *Blei;* Latin, *Plumbum.* Symbol, Pb; chemical equivalent, 207.—This metal was known at an early period, and is mentioned in the books of Exodus, Job, and Jeremiah. The Phœnicians obtained lead and tin from Britain, and CAMDEN states that lead was produced in Cumberland, Cornwall, and some other places, before the Christian era. PLINY designated the metal *plumbum nigrum*, to distinguish it from tin. Pigs of lead bearing Latin inscriptions have furnished abundant evidence that the Romans worked the British mines; whilst the Saxons have left traces of their industry in pursuit of the metal, as in the case of the mines near Castleton, in Derbyshire, one of which was dedicated to ODIN. The discovery of a sarcophagus of lead, which was lined with linen, has led to the fact that the mines near Wirksworth were worked before the year 714. The mines of the Peak and of the wapentake of Wirksworth were the property of the sovereign, and the district was known as the King's field.

Physical Properties.—The specific gravity of pure lead at 60° Fahr. is 11·445, BERZELIUS; ordinary lead, 11·358; when hammered it reaches 11·387. A freshly-cut surface of lead is bluish-white, not unlike polished steel, but it soon becomes dull by oxidation; losing its bright metallic lustre, it acquires a colour which is commonly defined as lead gray. It is the softest metal in common use; is easily cut with a knife, and scratched with the finger nail. Pure lead is very feebly sonorous, and emits a dull sound on being struck with a hard substance. The presence of a small quantity of impurities, especially antimony, imparts so decided a hardness, that the distinction of hard and soft lead in commerce is well understood to define the qualities in the market. Although as crystalline as tin, it yields no crackling sound on bending. The crystalline character may be observed on skimming the surface of fluid lead shortly before solidification, when beautiful fern-leaf forms of crystals are manifested. Upon gently raising the solidified crust from the fluid lead beneath, octahedral forms may be distinctly observed amongst the projecting crystals. Similar forms may be traced in the crystals obtained in the desilverizing process of PATTINSON described subsequently. The most striking view of the crystalline character of lead is obtained by heating a pig of lead upon the floor of a red lead oven, and when it has nearly reached the melting point breaking it with an iron paddle. The fracture thus obtained with pure lead presents an irregular columnar structure, somewhat like that of the starch of commerce. Indications of crystalline structure are also displayed etched upon the surface of lead left uncorroded in the operation of making white lead, and may be even traced on the portion of white lead detached.

At ordinary temperatures lead is very malleable, tough, and flexible. Its ductility is not great. Lead wire, of about one-sixteenth of an inch in diameter, is manufactured for gardeners' use for nailing trees to walls. When heated to a certain degree, solid cylinders or pipes may be squeezed out in continuous lengths.

According to REGNAULT, the specific heat of lead between 10° C. and 100° C. is 0·0314; for molten lead between 350° and 450° PERSON found it to be 0·0402. Lead is easily fusible; the melting point according to PERSON is 334° C., corresponding to 326°·2 of REGNAULT'S air thermometer. When pure it solidifies abruptly; but a very little impurity, such as antimony, tin, or sulphur, produces a pasty condition before solidification. The latent heat is such that 1 part by weight, in passing to the solid condition, evolves heat sufficient to raise 5·369 parts of water one degree C. Its conductivity for heat and for electricity, taking silver as 100, is 8·5 for heat, and 10·7 for electricity.

At a bright red heat fumes of oxide of lead are evolved, but lead cannot be distilled like zinc; at a higher temperature it burns with a livid flame. Though tasteless, the metal has a characteristic odour when rubbed between the fingers. Lead may be welded cold. The experiment is best made by cutting lead with a sharp knife, and pressing the clean surfaces together with a twisting motion. DOBBS obtained a patent in 1805 for producing the cohesion of tin and lead in this manner by passing the ingots through rolls.

Chemical Properties.—In dry air, free from carbonic dioxide, lead preserves a bright surface; but on exposure to the ordinary atmosphere it suffers corrosion by oxidation, and formation of the hydrate and carbonate. Rain water, and all soft waters, act upon lead, evolving hydrogen, and readily dissolve a small quantity of the hydrate. Lead dissolves in dilute nitric acid; with stronger acid, the action is arrested by the formation of white granular crystals of plumbic nitrate. It is but slightly attacked by either hydrochloric or sulphuric acid, unless concentrated and boiling. Pure lead leaves no insoluble residue in nitric acid. When antimony, tin, and sulphur are present, a white insoluble matter is left behind, consisting of the oxides of these metals, together with lead sulphate. If antimonic oxide predominates, the residue has a yellow tint.

There are three oxides of lead—PbO, PbO_2, and Pb_3O_4, or thus $(PO)_2PbO_2$, and a suboxide (diplumbic oxide) Pb_2O.

Plumbic Oxide, PbO.—Obtained by heating lead in air at a moderate heat, and constantly exposing a fresh surface for oxidation. The product is separated from the grains of unoxidized metal by grinding and levigation. It then presents the appearance of a brownish-yellow powder, called massicot. By heating white lead (plumbic carbonate) it is obtained of a clear lemon-yellow colour. At a heat a little above redness it melts, and crystallizes on cooling in yellowish-red scales, called litharge. Plumbic oxide dissolves in dilute nitric acid. Caustic alkalies also dissolve it sparingly. It is used for making lead salts, driers for paint, and for glazing pottery.

Triplumbic Oxide, Red Lead, Minium, Pb_3O_4.—This oxide is obtained by submitting powdered litharge to a regulated heat in suitable ovens, where by constant stirring it absorbs oxygen, and assumes a bright red colour. It is attacked by nitric acid,

which withdraws the protoxide, and leaves an insoluble puce coloured oxide, PbO_2. Red lead is completely dissolved if a little sugar be added to the dilute nitric acid. The commercial article generally contains a trifling residue of metallic lead and plumbic sulphate, besides such impurities as antimony, tin, and copper oxides, derived from the lead employed. By strongly heating it is converted into the yellow plumbic oxide.

Plumbic Dioxide, PbO_2.—This is a dark brown powder, used in the laboratory as an oxidizing agent. Hydrochloric acid decomposes it with the aid of heat, forming plumbic chloride and evolving chlorine.

Plumbic Nitrate, $Pb(NO_3)_2$, is a salt which crystallizes with facility from water. Its hot solution is capable of dissolving plumbic oxide, and upon this reaction a process for making white lead has been founded, the excess of oxide being precipitated by a current of carbonic acid gas. Nitrate of lead is used in the chrome yellow style of calico printing.

Plumbic Chloride, $PbCl_2$.—This salt may be obtained as a curdy white precipitate by the addition of hydrochloric acid to a solution of the nitrate or acetate. It is soluble in hot water, but only sparingly in cold. By slow cooling of a saturated solution it crystallizes out in characteristic needle-shaped crystals. At a moderate heat it fuses, and has the appearance of a horny mass when cold. A basic oxychloride, Pb_2OCl_2, is prepared on the large scale as a pigment, and known as oxychloride of lead paint. A still more basic compound is used as a yellow paint, and called Cassel yellow.

Plumbic Sulphate, $PbSO_4$, is a white salt, quite insoluble in water, but soluble in acids, potash, and many neutral salts, especially ammonic acetate.

Plumbic Sulphide, PbS, is precipitated from solution as a black powder by hydric sulphide. When the solution contains free hydrochloric acid, the precipitate is at first red, owing to the formation of $PbS + PbCl_2$, but this is soon converted into the black sulphide.

Plumbic Iodide, PbI_2, crystallizes from water in beautiful yellow scales. A soluble iodide forms an excellent test for the presence of a small quantity of lead.

Plumbic Oxalate, C_2PbO_4, is one of the most insoluble of lead salts in water, and is used in the quantitative analysis of solutions containing lead. It dissolves in nitric and hydrochloric acid.

The most characteristic tests for lead are the formation of black sulphide, the crystals of plumbic chloride soluble in hot water, and the yellow precipitate formed by soluble iodides or chromates. Heated on charcoal before the blowpipe with reducing fluxes, the compounds of lead yield a malleable bead of metal, and the charcoal immediately around the bead is at the same time coated with an incrustation of oxide, which is orange-coloured while hot, but becomes lemon-yellow on cooling.

Ores.—The chief ore of lead is galena or plumbic sulphide. The carbonate, sulphate, and certain phosphates and arseniates, are less important as sources of the metal.

Galena, Bleiglanz, PbS.—Occurs sometimes in fine crystals, generally cubical, the prevailing forms combining cubic with octahedral faces. The cleavage is very perfect on the cubical planes. Fracture conchoidal; opaque, lustre metallic; streak and colour lead-grey. Hardness, 2·5; spec. grav., 7·4 to 7·6. Pure plumbic sulphide contains—lead, 86·7; sulphur, 13·3. It is not unfrequently found with less than 1 per cent. of other substances. Silver is invariably present, and also minute quantities of gold. In some galenas the whole of the silver may be removed by washing, whilst other specimens treated in the same way part with very little silver, showing that the mode of existence of this metal in the galena is different. It is an error to suppose that large-grained specimens are less argentiferous. Galena melts at a strong red heat into a thin liquid, which rapidly penetrates clay crucibles. It readily volatilizes, and when oxygen is excluded condenses in a crystalline form. Cold dilute nitric acid decomposes sulphide of lead with formation of plumbic nitrate and separation of sulphur. Strong fuming acid converts it into sulphate. It is attacked by hydrochloric acid with formation of plumbic chloride and evolution of hydric sulphide. Plumbic sulphide may be melted with metallic lead in all proportions; but the product when cold appears to be a solidified solution of the sulphide in the lead. When more than 2 or 3 per cent. is melted with lead, unless it is cooled very quickly soft lead liquates out, leaving a pasty mass of mixed sulphide and metal.

Carbonate of Lead, Cerussite, Bleispath, $PbCO_3$.—This mineral occurs in crystals of the rhombic system, isomorphous with aragonite and saltpetre, or in fibrous, compact, and earthy masses. Hardness, 3 to 3·5; sp. grav., 6·4 to 6·6. In its purest state it is colourless and transparent as glass, with highly refracting properties. Its composition is lead oxide, 83·6; carbonic dioxide, 16·4. It effervesces with nitric acid, becomes black with hydric sulphide, and on charcoal is easily reduced before the blowpipe flame to a button of lead.

Sulphate of Lead, Anglesite, Blei-Vitriol, $PbSO_4$.—Resembles the carbonate in colour and lustre of the crystals, but is distinguished by the absence of effervescence with nitric acid. Before the blowpipe flame it melts to a transparent glass, which becomes milky on cooling. Its composition is lead oxide 73·7, and sulphur trioxide 26·3.

Phosphate of Lead—Pyromorphite.—This mineral exhibits a variety of colours between green, yellow, and brown—sometimes of a waxy yellow. Hardness, 3·5 to 4·0; sp. grav., 6·5 to 7·1, or slightly less when containing calcic phosphate. A proportion of plumbic chloride appears an essential constituent, and the phosphoric is sometimes partly replaced by arsenic acid, especially in the yellow varieties. Orange-red crystals from Leadhills contained plumbic phosphate 90·09, and plumbic chloride 9·91. Klaproth's analysis of a specimen from Wanlock Head gave oxide of lead, 80; phosphoric acid, 18; chlorine, 1·6. It is a brittle mineral, and crystallizes in forms derived from an obtuse rhombohedron. On

charcoal it fuses without reduction to a globule, which on cooling assumes a crystalline polyhedral form—hence its name.

Arsenate of Lead, *Mimetesite*, so called from its resembling pyromorphite; the crystalline form is, however, hexagonal, often occurring in barrel-shaped crystals. The colour is pale yellow, orange-yellow, or brown. Hardness and specific gravity similar to the last-named mineral. Analyses by Dufrénoy and Rammelsberg are as follows:—

	Cornwall.		Cumberland.
Plumbic arsenate,	84·55	....	71·70
Plumbic phosphate,	4·50	....	19·00
Plumbic chloride,	9·05	....	9·45

It is easily reducible on charcoal, giving off arsenical fumes.

Other ores are of interest chiefly to the mineralogist, as they do not occur in sufficient abundance to be worked for the metal. Amongst them are sulphato-carbonate and cupreous sulphate of lead, found at Leadhills and in Cumberland. Oxychloride occurs at Matlock and in the Mendip district. Vanadate, molybdate, and chromate are somewhat rare.

Distribution.—Lead ores are found in rocks of different geological age, from the granite and clay slates of the Devonian to the Triassic formations. Liskeard and Truro in Cornwall have been productive localities, the veins occurring in the clay slate or killas, as in the celebrated mines of Beer Alston on the Tamar. The Carboniferous series of Devonshire, or black slates, have yielded very little. In the Mendip Hills very productive lead mines are found in the Carboniferous Limestone formation. Lead lodes are abundant in the mountainous districts of Shropshire, in the original Silurian rocks, and in Cardiganshire; mines are worked in the clay slates and grit stones of the lowest Silurians. The mines of the Mountain Limestone formation are also in Derbyshire, Yorkshire, Cumberland, Northumberland, and Durham. In Scotland, at Wanlock and the Leadhills, and in the Isle of Man, the mines lie in the Silurian rocks. The granite district of Wicklow, Newtonards in County Down, and some other places in Ireland, furnish supplies of lead ore.

Lead mines in other countries enumerated in Ure's Dictionary are as follows:—Poullaouen and Huelgöet, in Finisterre; Villefort and Viallay, department of Lozère; Pezey and Macot, Savoy; Vedrin, near Namur; Saxony, The Hartz, Bleyberg in the Eifel; Villach, in Carinthia; in Bohemia, south-west of Prague; Tarnovitz, in Silesia; Joachimsthal and Bleistadt, on the southern slope of the Erzgebirge; Linarès, in the Sierra Morena; Catalonia, Granada, Murcia, and Almeira.

Many of these mines are highly argentiferous, and worked more for the silver than lead.

The total quantity of lead ore raised and sold in the United Kingdom, according to returns made to the Mining Record Office during 1875, was as follows:—

	Quantity.		Value.
Lead ore,	77,746 tons.	....	£1,202,148
Lead,	57,435 "	....	1,290,373
Silver,	487,358 ozs.	....	115,747

Summary of the produce of different counties—

	Lead Ore.	Lead.
	Tons.	Tons.
Cornwall,	2,566	1,932
Devonshire,	335	242
Somersetshire,	1,546	455
Derbyshire,	2,283	2,090
Shropshire,	7,932	6,039
Cumberland,	2,128	1,554
Yorkshire	4,049	2,945
Westmoreland,	1,646	1,106
Durham and Northumberland	22,304	16,525
Cardiganshire,	5,835	4,401
Montgomeryshire,	8,940	6,718
Denbighshire,	2,600	1,954
Flintshire,	3,003	2,214
Carnarvonshire,	1,408	1,046
Isle of Man,	4,429	3,158
Ireland,	1,850	1,387
Scotland,	4,109	3,078

The high specific gravity of the ores of lead renders the operation of dressing and washing them from the earthy matters comparatively simple. In most cases the cleansing is done contiguous to the mine, and the finer particles separated from the ore by iron wire sieves placed in water. A common method is to lead a stream of water on to a grate upon which the lumps of stone are washed, and the metallic parts carried through on to an inclined plane, which leads to a trough in which the better quality of ore collects, whilst the slimes are carried forward and recovered in suitable settling troughs. Thus it is easy so to dress ore as to obtain 80 to 83 per cent.

Metallurgy.—*Lead Assay.*—The ores of lead for the purpose of assay may be divided into two classes. The first are the oxidised ores—carbonates, sulphates, and phosphates; the second are the galenas, with ores containing arsenic and sulphur. The fluxes and reducing agents required for the first class are dried carbonate of soda and finely divided carbon or lampblack. A little borax is useful when the proportion of basic substances is large. When much sulphate of baryta is mixed with the ore fluor spar will be found to yield an easily fusible slag.

With the second class of ores metallic iron is the best reducing agent, with or without a small proportion of carbon, and with sufficient sodium carbonate to flux the gangue or earthy matters accompanying the galena. The assay furnace, convenient for lead assays, is about 10 inches square internally, and the height from the fire-bars to the horizontal flue leading to the chimney about 14 inches. The chimney should be at least 20 feet high, and dampers to check the draught at the proper period should be provided, either by closing the ash-pit with a regulator, or by means of a door in the breast of the chimney. The most convenient fuel is hard coke broken into pieces about 2 inches diameter. If clay crucibles are used they should not be too wide. Wrought-iron crucibles with a thick bottom are by far the best for the assay of galenas; they should be forged out of a short piece of round bar iron by hammering it hot over a core or mandril. A useful size is 4½ inches in height, 3 inches diameter at the top, and 2¼ at bottom, which is nearly 1 inch thick.

This size will conveniently carry 1000 grains of ore, and the necessary flux for such a quantity.

The assay charges for such crucibles should be as follows:—

Ore,	500	grains.
Sodium carbonate,	500	"
Cream of tartar,	50	"

For poorer ores a portion of the sodium carbonate is advantageously replaced by borax. The ore being mixed with four-fifths of the bulk of the flux, is placed in the fore part of a suitable copper scoop, with the remainder of the flux immediately behind, so that in transferring it to the pot the charge may have a covering of flux alone. When borax is used it should not be mixed with the charge, but put on the top in the same way. The crucible is first heated to dull redness, taken out of the furnace, and the charge shot into it from the scoop, taking care to brush all particles adhering to it into the pot. When placed in the furnace the heat should be very gradually raised from dull to full redness, until the contents are in a state of tranquil fusion. At this stage it is well to inspect the inside of the crucible, to see if any matter carried up by the bubbling of the flux may not be adherent to the sides of the pot; and if this is the case it must be pushed down, by means of a hot stirrer, into the melted mass, after which the furnace is kept closed for a few minutes. When the crucible is removed from the furnace, care must be taken not to pour out the contents too hot, as a film of lead is then apt to remain on the surface of the iron instead of running into globules. The melted lead and flux are received into an ingot mould, previously warmed and rubbed over with plumbago, after which the pot is again examined, and if any shots of lead are observed they may be brought together by a smart tap of the inclined crucible on the top of the furnace, and poured into the ingot mould. It may be sometimes necessary to throw in a little sodium carbonate and cream of tartar, and to return the crucible to the furnace for the complete fusion of the residual matter, and then to pour out to recover the remaining lead.

After solidification and cooling, the button of lead is readily detached from the slag by striking it sideways on a slab of iron. If any particles still adhere to the metal after hammering, they may be removed by scrubbing with a brush and hot water. When a clay pot is used it is necessary to supply the iron for the formation of sulphide in the form of nails, or a bent piece of hoop iron. The nails, about 3 inches long, should be placed with heads downwards, and the ore, mixed with its own weight of sodium carbonate, should be pressed tightly about the nails and covered with a layer of borax. The assay is then conducted, as in the former case, by bringing the pot gradually to a red heat. When perfectly fluid, the nails or iron are seized with the tongs and carefully washed in the liquid slag until free from adhering lead. It is a good plan to smear the inside of the crucibles with common black lead, and to make a second assay for verification.

All the ores of lead may be assayed in clay pots; but the oxidised ores do not require metallic iron, which is only to be used when sulphides and arsenides are present. Carbon, however, must be added to reduce the oxide of lead, and may be used in the form of lamp black, finely-powdered charcoal, or cream of tartar. The button of lead obtained by the various methods of assay always contains greater or less proportions of other metals which may accompany the lead ore, such as copper, silver, antimony, or tin. For commercial purposes it is not necessary to subject the lead to a chemical examination, but its purity is usually judged of by its colour and softness.

When galenas contain much antimony, they should be assayed in an open clay crucible, with three times the weight of sodium carbonate. The lead will be reduced, whilst the antimony, becoming oxidised, unites with the alkali, and remains in the slag. If assayed in an iron pot, both metals will be liberated, and yield a button of hard lead.

Assay of Lead Ore for Silver.—The value of lead ore and lead can only be estimated when the amount of silver is also determined. For this assay, the buttons of lead obtained in the valuation of the lead ore can be at once used for the estimation of the more precious metal. In the reduction of the lead all the silver contained in the ore will be found in the metal, even if the assay is continued so long as to allow of considerable loss of lead by oxidation.

The furnace for the silver assay consists essentially of a ⊐-shaped retort of fire-clay, called a muffle, which is closed at one end, the opening of the other end, which is set in the face of the furnace, being closed with a movable piece of clay, which may be furnished with a hole to afford means of watching the progress of the assay. The muffle is placed either on fire-bricks or bars, in such a manner that it may be equally heated all over. The fuel may be either coke or coal. Small cup-shaped supports, made of bone-ash, called "cupels," are placed in the muffle until red-hot; the button of lead is carefully placed in them, and the heat kept up to a bright red. The lead at once melts, and commences to form litharge (PbO), which is absorbed, when melted, by the porous substance of the cupel. The button of lead diminishes in size, until at last the film of lead oxide on the metal, showing iridescent colours, disappears, and the phenomenon of "brightening" ("blicken") of the assay takes place. The operation is now complete, and the bead of silver, which may also contain gold, is covered by another hot cupel to prevent sudden cooling, which might cause the metallic globule to spirt, and a portion of it to be lost. When cold the bead is removed by pliers, cleaned with a stiff brush, and weighed.

Smelting.—According to the class of ores treated, the smelting operation consists of desulphurisation of galena, or deoxidation of oxidised ores, or both operations are combined.

1. When plumbic sulphide is heated in air, it may be oxidised, and a roasted charge of ore will contain plumbic oxide and plumbic sulphate. If it

be now intimately mixed with sulphide of lead, in such a proportion that the oxygen in the roasted ore is equivalent to the sulphur in the unoxidised galena, to form sulphurous dioxide, complete reduction of the lead will ensue. This reaction is exhibited in the following chemical equations :—

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The term *air-reduction process*, or the German roast-reduction process, may be applied, as it suggests the agent by which the removal of the sulphur is effected.

2. The roasting or calcination may be continued, and the subsequent reduction of the oxidised products effected by carbonaceous matter.

3. When metallic iron is employed as an agent for desulphurisation, the term precipitation, or *iron-reduction process*, is used.

In some cases all these processes are employed in combination ; and in the reduction of the oxidised ores both carbon and iron are employed as agents of reduction.

In the air-reduction process both kinds of furnaces are in use—reverberatory and blast. In the Flintshire furnace and the Spanish furnace, or *Boliche*, the lead is allowed to accumulate in the furnace, and is tapped out. The residue is raked out in pasty lumps, and is called grey slag or drawn slag ; or in certain cases is tapped out in a molten state, when it is called run slag. When the flowing furnace is used, the ore is calcined in a separate furnace. The slags in this case are run out in a molten state. At Bleiberg the lead runs out of the furnace as soon as it is reduced. The residue is pasty, and the lead contained in it is extracted from it in the same furnace. The blast furnace, called the ore hearth, is used also for the air-reduction process, when calcination and reduction of the ore occur *pari passu*, and the residue is raked out in pasty masses.

Flintshire Process.—The following distinct operations are comprehended in this operation :—

1. Calcination at a regulated heat, to produce a certain amount of oxide and sulphate of lead.

2. Raising the temperature to cause fusion, and determine the liberation of the lead by the reaction of the oxide and sulphate upon the unchanged sulphide.

3. Addition of lime and incorporation with the charge, now becoming too fluid to allow the reaction to continue. At this stage an excess of oxidised products are formed, and small coal is sometimes added.

4. Tapping the reduced lead, and subsequent removal of the grey slag by drawing or tapping.

The furnace employed for the reduction of lead ores by the Flintshire process varies somewhat in its construction and dimensions. The length of the hearth is usually about 11 feet, and its width 9 feet, built upon an arched vault extending the whole length of the bed to the fire-bridge. The hearth is made of slags, moulded into the proper form when in a plastic and semi-fused state. Towards the centre of the bed there is a depression for the metal to accumulate, at the bottom of which is the tap-hole. The fire-place is at one end, having a grate about 6 feet by 4 feet in area. Before reaching the bed of the furnace, the flame passes over a fire-bridge about 2 feet in width, and from 12 to 14 inches below the arch. At the opposite extremity of the hearth are openings communicating with the flue in connection with a lofty chimney. The fire-hole for charging coal is at the back, and the grate is freed from clinkers, or cleaned, at the front. Six working doors, usually about 9 by 12 inches, are placed in strong cast-iron frames set in the sides of the furnace, with a slight inclination inwards. The slag bottom is made nearly level with the doors on one side, but is inclined towards the other in such a way as to be from 18 to 20 inches below the middle door where it communicates with the tap-hole. A

Fig. 1.

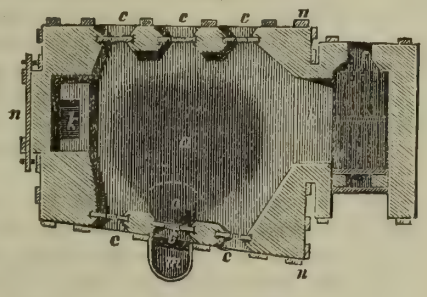
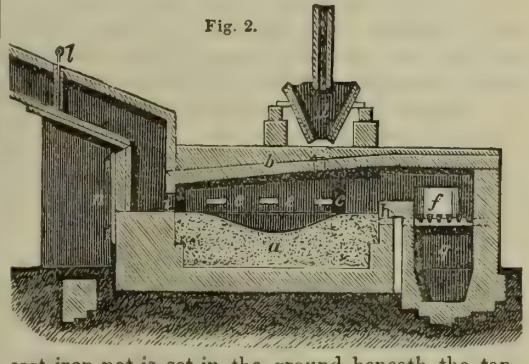


Fig. 2.



cast-iron pot is set in the ground beneath the tapping hole, and on the top of the furnace is a large hopper for charging the ore. The best slags for forming the bed are the ordinary grey slags, of which about 5 tons are required for one bottom. The true working bottom varies in thickness from 6 to 12 inches, being thicker towards the tap-hole. An open space is left for the free circulation of air between the inner fire-place wall and the adjacent end wall of the bed. The whole furnace is stiffly braced together by wrought-iron standards and tie-rods. Figs. 1 and 2 are illustrations of a Flintshire reverberatory furnace ; *a* is the bed ; *b*, arched roof ; *c*, *c*, *c*, working doors ; *e*, grate ; *f*, fire-door ; *g*, ash pit ; *h*, fire-bridge ; *i*, opening to chimney, *k* ; *l*, damper ; *m*, pot ; *n*, tie rods and standards ; *o*, depression in the bed.

Process of Smelting.—The usual charge for the fur-

nace is 21 cwts. of dry ore, which is let down from the hopper and spread evenly over the bed, care being taken to prevent it dropping into the deepest part, or well, of the furnace.

At first the furnace is barely red hot after working off the previous charge. The ore is now frequently stirred and turned over for two hours; the temperature being regulated by the damper, and the doors left open, or only partially closed, in order to admit the requisite quantity of air. Constant stirring, and the highest temperature compatible with the absence of pastiness or clotting, are the essential conditions of this roasting stage. At the end of two hours the grate is freed from clinkers and filled with coal, the fire is urged until the charge becomes semi-liquid, and any portion of it which may have run down towards the tap hole is raked up to that which remained on the upper part of the furnace bed. The fire door is now opened, and the temperature lowered until the charge acquires the consistency of a stiff paste, when the whole of it is pushed towards the bridge and back part of the furnace, opposite the tap hole side. When this is done the fire-door is again closed, and the charge melted down as quickly as possible into the well; slaked lime in powder is then thrown in, and well raked over the surface of the melted mass.

The slag and unreduced portion of ore being thus rendered sufficiently stiff are again thrown up, or, as it is termed, "set up" on the sloping sides of the bed, there left to cool a little, and afterwards remelted. Lime is again added, the slag is pushed back from the surface of the lead and left to drain a little; the lead is tapped, and the slag afterwards raked out of the furnace in pasty lumps called "grey slag."

Variations of temperature and manipulation are required to suit particular ores. The time usually occupied in working off a charge is five hours. Rapid fusion of the set up charge lessens the loss of lead by volatilization. A satisfactory calcination will always yield the best results, the first stage of the process being highly important. The quantity of fuel varies with its quality and the nature of the ore. The minimum may be estimated at 12 cwts., and the maximum 16 cwts.

Percy, from whose work much of this description is drawn, states that 21 cwts. of good Flintshire ore yield about 14½ cwts. of lead, and of this quantity about 91 per cent. of the lead is obtained direct from the furnace, and 9 per cent. from the slag and fume. The ores treated yield by dry assay from 75 to 80 per cent. of lead.

The following analytical data from smelting lead ore at Bagilt are given in Percy's "Metallurgy:"—

	Ore calcined 2 hours.	Grey Slag after tapping.
Sulphide of lead,	53·79	—
Sulphate of lead,	2·84	18·73
Protoxide of lead,	36·87	38·08
Oxide of zinc,	2·65	12·00
Lime,	1·63	13·50
Protoxide of iron,	0·90	3·89
Alumina,	—	0·71
Silica,	1·10	12·32
	99·78	99·23

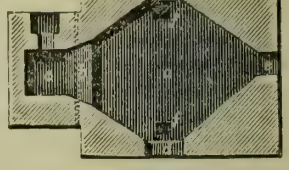
The quantity of grey slag produced per charge is nearly 4 cwts., and yields from 53 to 55 per cent. of lead; it is subsequently treated in a blast furnace.

In Derbyshire the furnace used for smelting lead ores is similar to the furnaces of Flintshire; but is smaller, and has two tap holes, one for lead and the other for slag. The charge is 16 cwts., and is worked off in 4½ to 5 hours. The slag is tapped off, and amounts to 3¼ cwts., containing about 8 to 10 per cent. of lead. Occasionally some "drawn slag" is produced. The matrix of the Derbyshire ore usually contains sulphate of baryta and fluor spar, and when much of the former mineral accompanies the ore fluor spar is purposely added, as these substances intermixed readily melt into a thin liquid, so that the slag can be easily tapped. This run slag is compact, opaque, earthy in fracture, and yellowish or brownish grey. From its vesicular character it was formerly termed "macaroni-slag." The following analyses of slags from the Lea Smelting Works, near Matlock, are given by Berthier.

	Run Slag.		Drawn Slag.	
	1	2	1	2
Fluoride of calcium,	16·0	13·6	7·2	8·5
Sulphate of baryta,	25·0	30·0	22·0	24·4
Sulphate of lime,	22·5	33 0	1·6	5·6
Sulphate of lead,	22 0	9·0	12·0	30·0
Oxide of iron, } 4·5		2·0	15·4	5·6
Oxide of zinc, } 4·5		2·0	7·2	8·0
Lime,	8·0	8·8	14·0	14·7
Galena,	—	—	17·6	2·0
Carbonic acid and loss,	2·0	1·6	3·0	1 2
	100·0	100·0	100·0	100·0

In Cornwall, at the Smelting Works at Par, and at Point on the Truro river, the reduction of the ore, which is an impure galena, is effected in two operations requiring separate furnaces. The first process is the calcination of the ore in the calciner—a reverberatory furnace with flat bed, having three doors, one on each side, and the third at the end near the stack. A square hole in the bed is adjacent to each of the side doors, for the purpose of raking out the roasted ore into the arched vault beneath. Fig. 3 is a plan of a Cornish calcining furnace, of which *a* is the bed; *b*, fire-bridge; *c*, fire-place; *d*, *d*, working doors; *f*, *f*, holes for raking out the charge; *e*, smaller working door. The charge is from 1¼ to 2 tons, assaying from 65 to 70 per cent, and a great part of it being in fine division as it is dressed and obtained from the "sieve beds." The calcination is carried on for fifteen or twenty hours, the ore being turned over once an hour, with occasional addition of lime to prevent clotting. About 6 cwts. of coal are consumed per ton of ore. The next process is carried on in the "flowing" or "melting" furnace, which is only a modification of the Flintshire furnace. Fig. 4 is a plan of a Cornish flowing furnace; *a* is the bed, inclined

Fig. 3.



towards the tap hole, *b*; *c*, fire-place; *d*, *d*, *d*, and *h*, working doors—under the working door, *f*, is an iron

Fig. 4.

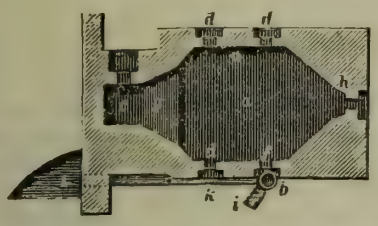


plate with slit for the tap-hole; *g*, fire-bridge; *k*, channel for slag to run into *l*; *i*, receptacle for matt. The charge in this furnace is 2 tons of calcined ore, which is at first spread over the sloping bed, and the doors closed. The heat being raised, the charge is melted in two to three hours, and with good ores the reduced lead is tapped off at this stage. The liquid charge is now set up with lime and "culm"—*i.e.*, anthracite—and again spread over the bed. Fluor spar is sometimes used as a flux; and from 1 to 2 cwts. of scrap iron are placed in the furnace at the tap-hole, with the object of decomposing the sulphide of lead. The doors are again luted, and the charge fused. Upon tapping, the lead flows into the pot, followed by a regulus composed chiefly of sulphide of iron. When slag begins to run, the tap-hole is enlarged and the lip of the pot stopped up with ashes, so as to direct the flow of the slag along a gutter which conducts it to a large pit outside the smelting house. The operation lasts eight hours, with a consumption of 8 to 9 cwts. of coal per ton of ore. The slag is generally sufficiently free from lead as to admit of its being thrown away. Most of the copper passes into the regulus, which requires subsequent treatment.

The lead obtained is usually so hard as to require softening by calcination at a red heat, whereby the antimony, which is the chief cause of the hardness, is oxidised.

At Alport, in Derbyshire (the works are now closed), the sweepings of the condensing flues were smelted in the reverberatory furnace, and produced a very excellent quality of lead, which was called soot lead. The soot was charged in the form of a stiff mud, and when dried and melted was set up with small coal and lime. The Flintshire furnace and method of working here described are in use, with unimportant modifications, at the Friedrichshütte, at Tarnowitz, at Couëron, Loire Inférieure, and in Spain and Belgium.

The Spanish reverberatory furnace, or "boliche," has the form of a rectangular prism, and until very lately was worked with fuel consisting principally of ilex and gum cistus of about four years' growth. At La Fortuna, Linares, the process is divided into three operations:—1. Caldeo, or calcination, lasting from one hour to an hour and a half; 2. Blandeo, sweating or roasting, for four and a half hours to five hours; 3. Corrida, running down, which occupies the remainder of the eight hours' shift.

Carinthian Process.—At Bleiberg the ore is smelted in a reverberatory furnace of unusual construction. The bed slopes regularly from one end to the other, and from each side towards the median line; the fire-place is parallel to the long axis of the bed; the grate is of stone, with four or five openings for the admission of air. Wood is generally used as a fuel, but in some instances brown coal. The charge is not more than 300 lbs.; and the mode of conducting the operation can be divided into three stages, namely—1. Roasting, for oxidation of the plumbic sulphide, and formation of oxide and sulphate; 2. Rabbling the charge *(Bleirühren)*, so as to bring about the reaction necessary for a flow of lead; 3. Reduction of the oxidised compounds in the slag *(Bleipressen)*. This is accomplished by mixing with the liquid grey slag a quantity of small charcoal and ashes; and after setting up the charge on the bed, the heat is got up considerably, and another flow of lead obtained. A quantity of slag, amounting to about 90 to 100 lbs., called gekrätze, is left behind, which is stamped and washed for further treatment, and which may contain 50 to 60 per cent. of lead. The lead produced is known in commerce as "Villacher blei," and is classed amongst the purest and softest kinds. Streng gives the following analysis:—

Lead,	99·9660
Copper,	trace.
Iron,	0·0039
Zinc,	0·0041
Antimony,	0·0260
	100·0000

The lead obtained during the first period of the operation is of better quality, and is called "jungfernblei." According to Eschka, in 1874, the composition at the two periods was the following:—

	Köstperiode, or Calcination.		Pressarbeit, or Slag Reduction.
Copper,	0·00069	....	0·00075
Silver,	0·00025	....	0·00025
Antimony,	traces.	....	0·00703
Arsenic,		....	0·00721
Iron,	0·00055	....	0·00088
Nickel,	—	....	trace.
Zinc,	0·00076	....	0·00082
Sulphur,	0·01476	....	0·01785
Lead (by difference),	99·98299	....	99·96521

Smelting Lead Ore in Blast Furnaces.—The *ore hearth*, or Scotch furnace, is a small rectangular blast furnace or hearth, composed of pieces of cast iron set in brick work or stone. Figs. 5 and 6 represent the ore hearth. It is contained within a chamber of masonry inclosing the hearth, and forming a hood over it which communicates with the chimney, leaving it open only at the front. The hearth itself is composed of twelve pieces of cast iron; *g*, hearth-bottom, 22 inches square, the bottom 3 inches thick, and the sides 3 inches thick and 4½ inches deep. Between the hearth-bottom and the brick or stone bed on which it rests is usually interposed a layer of sand a few inches thick. The work-stone, *m*, is shown sloping 3 inches or 4 inches from the front edge of the hearth-bottom; it is 3 feet long, 1½ foot broad, and 2½ inches thick. It has a raised border 1 inch high on its two sides and in front,

with a channel 2 inches wide and 1 inch deep running diagonally across it. The space between the under surface of the work-stone and the brick or stone bed is generally filled up with fire-clay, or with a mixture of slime-ore and bone ashes duly tempered with water. *b*, bearer, a square prism 6 inches on the side and 26 inches or 28 inches long; there is one on each side. They overhang somewhat the sides of the hearth-bottom, and so tend to keep it firm in its place; if they are made full long they can be turned when worn at one end: *a*, backstone, a prism 28 inches long, 6½ inches high, and 5 inches broad; the bellows-pipe rests upon this piece. *f*, pipe-stone, a prism 10 inches square and 28 inches long, with an opening on the under side to receive the bellows-pipe. *e*, upper backstone, a prism 28 inches long, 4 inches high, and 5 inches wide, which completes the back of the hearth. *d*, forestone, a prism 26 inches long, 6½ inches high, and 5 inches

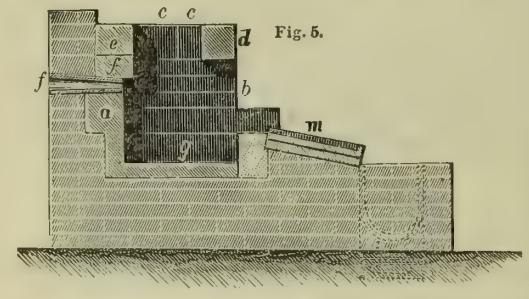


Fig. 5.

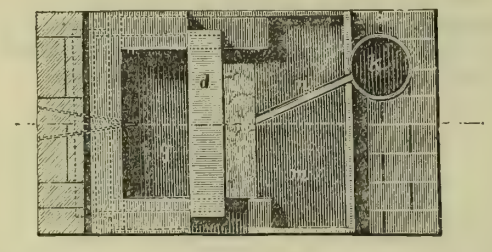


Fig. 6.

broad. *c*, *c*, keystones, exact cubes, 10 inches on the side; there are two on each side. The two nearest the back are placed upon the bearers, *b*, so as to be level with them on the inside, and they are therefore 22 inches apart; but the two in front are made to lie against the ends of the forestone, *d*, and they are therefore 26 inches apart. *k*, pot of cast iron to receive the lead as it trickles down the channel, *n*, in the work-stone. The forestone is movable to a certain extent, and can be placed nearer to the backstone, or raised by the insertion of fire bricks at each end between it and the bearer. The bellows-pipe enters the hearth 6½ inches above the level of the upper end of the work-stone; but when the furnace is in work it is often not more than 4 inches above the surface of the lead. Sometimes the hearth is made 10 inches deep, so as to increase the quantity of lead returned in it, and thus lessen its tendency to get too hot during the process of smelting. We are indebted to H. Pattinson for an excellent account of this furnace, and the mode of working, which appeared in the "Transactions of the Nat. Hist. Soc. of Northumberland, Durham, and Newcastle-on-Tyne" in 1831. Two men are employed, and a shift lasts eight hours. The fuel is coal and peat cut into prisms 9 inches to 12 inches long, and 2½ inches square. The agglomerated mass of ore, slag, and coke left at the end of each shift is called the "browse," and the hearth, when in working order, should have the bottom nearly full of lead after the last shift. The mode of working is as follows:—"A small quantity of coal is spread on the lead in the hearth, which is then filled up with peats, well stacked up in front, while smaller pieces are thrown in behind. Some ignited peats are then placed before the nozzle, and the blast let on. When the fire has got up, more coal is added, and a little of the browse from the last shift is thrown behind the forestone. When the browse is worked in, lead begins to flow; the workman stirs up the contents of the hearth with a poker, throwing them forward away from the blast on the work-stone. At this moment the nozzle is cleaned from any slag, and a peat placed in front of it to disperse the blast and keep open the fire. The workmen now put back the portions of the charge which have fallen on the work-stone and set up the contents of the hearth, so that the blast is well distributed, adding ore in small quantities where the fire seems hottest. Lead now flows freely. The stirring up of the charge is repeated at intervals to diffuse the blast, and each time a fresh peat is placed before the nozzle of the bellows. From the portions which fall out on to the work-stone lumps of grey slag are picked out and laid aside for subsequent treatment. The pieces of browse are broken up and returned to the hearth, after which fresh ore is added. When the receiving pot is full of lead it is skimmed and ladled into pig moulds. Towards the end of the shift no fresh ore is added, but the browse is worked up alone, and at last, when the blast is stopped, it is taken out and separated from the grey slag, while some of the lead in the receiving pot is ladled back into the hearth-bottom, so as to fill it for the next shift. The process will be seen to be essentially an air-reduction process; the object being to oxidise the ore, and then to intermix with it fresh ore to obtain the reaction explained above. It will be noticed that the bed upon which the charge rests is fluid lead. Within comparatively recent periods the ore used was only subjected to careful dressing and mechanical treatment before smelting; lately it has been found advantageous to subject them to calcination, so as to remove a portion of the sulphur and to agglutinate the slimes, in order that they may resist the force of the blast without being carried up into the flues in the form of dust.

American Ore Hearth.—Figs. 7 and 8 are illustrations of this furnace; *a* is the lead reservoir; *b*, working plate, with channel conducting to the lead-pot, *c*; *g*, hollow iron jacket in which the wind enters at *d*, and then through *e* to the tuyer at *f*. This furnace was first introduced at the Rossie mines, in the State of New York, and was tried

at Bleiberg, in Carinthia, and Przibram, in Bohemia, but has now been abandoned. The fuel was wood. The furnace differed in dimensions from that

Fig. 7.

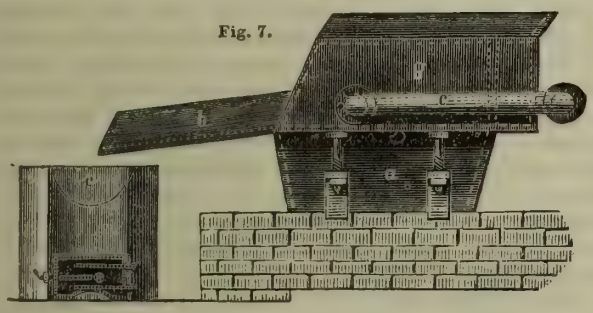
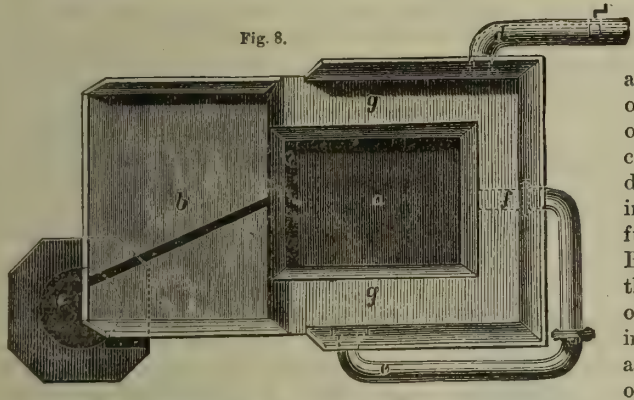


Fig. 8.



described above, and the air was led into a chest surrounding the hearth so as to keep it cool, and at the same time to furnish a heated blast and

Fig. 9.

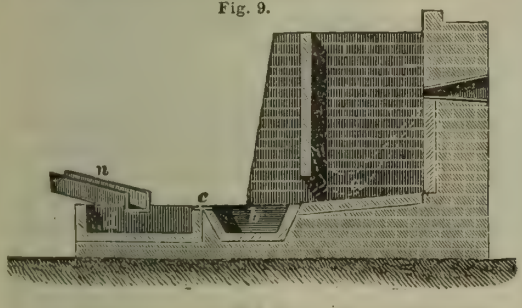
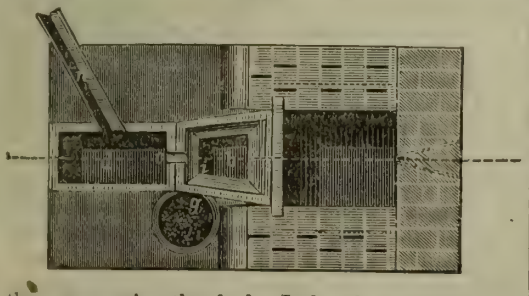


Fig. 10.



thus economize the fuel. It has been stated that 1 ton of wood was consumed for 2·6 tons of lead; the pressure of the blast was equal to a column of water 15 to 22 inches high. At Przibram, in 1856, ore containing 74·88 per cent. of lead yielded 60·68 per cent., exclusive of that subsequently recovered from the slags. In twenty-four hours from 60 to 74 centners of ore were treated, with a consumption of 53 4 cubic feet of wood, and 50·1 cubic feet of charcoal.

Slag Hearth.—When the slags resulting from the treatment of lead ores are not worked up in the smelting furnace itself, as in the Bleiberg process and the Cornish furnace, they are reduced in a special blast furnace called the slag hearth. This furnace is furnished with one tuyer only, and has the form of a deep hearth, or shallow rectangular furnace, answering to the *krummofen* of the Germans, and the *fourneau à manche* of the French; as shown in Figs. 9 and 10. It is made of fire brick and cast iron encased in common brickwork or stone, leaving an opening in front. The outer casing is prolonged upwards, and connected with a long flue for suitable condensation of the lead-fume. A plate of cast iron forms the bed-plate at the bottom of the furnace, and slopes downwards and forwards. Blocks of cast iron, named bearers, carry the side walls, and at the front is a plate of iron or forestone placed so as to have an interval of 7 inches between its lower edge and the bed-plate. The back is formed of another plate of iron below the tuyer. In front of the bed-plate is a trough of cast iron called the lead-trough, *b*, sometimes divided by an iron partition into two unequal parts; the larger one immediately in front, and the smaller one on the left. There is a hole at the bottom of the partition, through which molten metal may flow from one part into the other. The trough is cast in one piece. A slag pit, *d*, is also formed in the ground, in front of the furnace, into which water is conducted by the channel *n*. The outer brickwork below, which surrounds the hearth, is supported by cast-iron plates braced together with wrought-iron tie rods; the tuyer passing through the cast-iron plate which supports the back-stone, on which the nozzle rests. Above the hearth, in front, is an open space arched at the top; and a similar arched opening, but smaller, is made in the left wall for charging. The bed-plate is covered with a layer of hard, burned, and coarsely-sifted coal ashes, to within an inch below the nozzle of the tuyer, forming an ash bottom which slopes with the bed-plate towards the lower edge of the forestone. The space in front of the ash bottom between the bearers is plastered up with clay. The ash bottom acts as a filter to separate the lead from the slag, the latter running out over the ash bottom through openings made in the clay-stopping, while the lead percolates through the ash bottom to the bed-plate, and runs down to the lead trough. The larger division of the lead trough is filled with porous cinders, which also act as a filter, causing the slag to flow over into the slag pit, which is filled with water, while the lead

runs through the bottom and finds its way to the smaller division, when it is ladled out.

The lead which is produced is known as slag lead, and is whiter in colour and much harder than ore lead. The slag, named black slag, is vitreous, and is thrown away. The fuel is coke and peat. The shift lasts eight hours, during six of which the blast is continued, while two hours are consumed in preparing the furnace and emptying it at the close of the shift. The hearth is lighted with peats, and then charged with about 1 cwt. of coke. When the fire is well burned up, more coke and a little of the browse left from the previous shift are added. As it becomes hotter the hearth is charged with grey slag, and sometimes a little black slag and browse are thrown in until the slag begins to melt. An opening is then made in the centre of the clay-stopping with a pointed bar of iron. The slag now flows freely, and the hearth is kept supplied with fuel and material. Sometimes iron slag from puddling and re-heating furnaces is found useful when the grey slag contains much lime, the basic silicate of protoxide of iron forming with it a more fusible compound. In cleaning out the furnace a good deal of the material of the hearth and clay-stopping slagged together is cut out, and laid aside to be worked again. The quantity of slag smelted in a given time varies with the quality of the material. As an example of actual work, 80 cwts. of grey slag were passed through in six hours, with a consumption of 9 cwts. of coke, producing 18 cwts. of lead.

The Spanish Slag Hearth. — This furnace was originally designed especially for the treatment of Roman lead slags. It is circular in plan, with a sloping bottom, and is blown by three water tuyers. The shaft is built of single arch fire-bricks, and tapers somewhat at the upper part. There is an arched opening in front, and a breast pan of cast iron, which is rather deeper than semicircular in plan, and is open at the top and bottom. The breast pan has a slit, in which a tap-hole may be made higher or lower as required, and a notch in front on the top for a poker to be thrust into the interior of the furnace. The breast pan is filled with riddled cinders, and answers the purpose of the lead trough in the English slag hearths. The shift lasts twelve hours, during which about 7 tons of slag are smelted. In smelting 84 tons, yielding by dry assay about 8 per cent. of lead, 10 or 12 tons of coke are consumed. Forge cinders, scrap iron, and fluor spar are used for fluxes, as occasion requires. Any regulus which collects on the top of the lead is taken off and worked over again. At Alport in Derbyshire this furnace was found to yield excellent results, but it is not so well suited to the smelting of the richer grey slags produced in the Flintshire furnace. The rough lead was softened by throwing it on to the bed of a reverberatory furnace, where the soft lead was liquated out at a moderate heat. This operation was termed "kettling."

Castilian Furnace.—This furnace is circular, usually about 3 feet in diameter, and is constructed of fire-bricks. Its height is about 8 feet 6 inches, and the thickness of the walls is 9 inches. The breast is formed by a semicircular iron pan, furnished with a lip for running off the slags, and a longitudinal slot for tapping. On the top of the cylinder of brick-work is a box-shaped covering of masonry, supported by a cast-iron frame resting on four pillars. In this is placed a door for feeding, and the outlet by which the flame escapes into the chimney. The bottom consists of a mixture of fire-clay and coke dust, slightly moistened and well beaten in to the height of the top of the breast pan, which may be about 3 feet above the level of the floor. Above the breast pan an arch is turned, so that when the breast has been built up it may form an interval 18 inches wide and about 2 feet high. When the bottom has been properly beaten up to the required height, it is so hollowed out as to form an internal cavity communicating freely with that of the breast pan, which is likewise filled with brasque and hollowed to the depth of the internal basin of the furnace. The blast is applied by means of three water tuyers 3 inches in diameter at the smaller end, and 5½ inches at the other extremity, into which the nozzles are introduced. The blast is obtained by a fan, and conveyed to the tuyers through brick channels formed beneath the floor of the furnace-house. The fore-hearth is constantly kept covered by a layer of coke dust and cinders, and the slags flow continuously from the breast pan, through a spout which conducts to cast-iron wagons in the form of inverted truncated pyramids, of which the larger base is about 2 feet square. When a sufficient amount of lead has accumulated in the bottom of the furnace, it is tapped into an iron pot by removing a plug of clay in the slot of the breast pan, and after skimming from dross or matt of sulphides, it is ladled into moulds. The slag which is received into the waggons, when solidified, is tipped out, and if any lead or matt has collected at the bottom, it is readily detached when the matt is sufficiently cold. It is not found advantageous to work charges containing much more than 30 per cent. of lead. The coke should be thrown in the middle, while the ores and slag are spread next to the brickwork. By this method of charging the sides of the furnace are prevented from becoming too hot. The consumption of coke is about 2 cwts. to the ton of material smelted, and the black slag should not contain above 1 per cent. of lead. Scrap iron is occasionally used, especially when sulphides are present in the charge. The mouth of the furnace should be kept covered with fresh material, so that no flame may appear, as the cooler the furnace is worked, provided the slag is quite fluid, the less loss there will be by volatilization. In any case, it is important that the condensing arrangements be as complete as possible. Large heaps of old slags found in Derbyshire have been smelted in these furnaces, the assay of which was frequently only 8 per cent. of lead, of which 3½ only were obtained directly in the metallic form, the rest being recovered from the lead soot which was subsequently reduced in the reverberatory furnace. If galenas are smelted in these furnaces, they are better treated by previous

calcination; but if smelted in the raw state, metallic iron must be added.

Iron-reduction Process (*Niederschlag-arbeit*).—In various places on the Continent the lead ores are too poor to work with advantage in reverberatory furnaces, and are smelted with metallic iron, or some ferriferous material, in blast furnaces. When the ores are siliceous, as at Clausthal, this method is employed. The charge consisted of 34 quintals of ground ore and schlich, equivalent to 24 quintals of pure galena; 4 to 5 quintals of cupel bottoms, strongly impregnated with litharge; 1 quintal of "abstrich," or impure litharge, formed on the surface of the cupel; 39 quintals of slags derived either from the first fusion of the mineral treated, or from the remelting of matts; 4½ quintals of granulated cast iron. The fusion is conducted in a small blast furnace of from 20 to 25 feet in height, and about 3 feet square in the widest part. Figs. 11 and 12 represent the Clausthal furnace; s is the fire-brick or sandstone bottom; *g*, brasque; v, fore hearth; *n*, tap-hole; *o*, pot; *r*, opening in front; *q*, smoke funnel; *i*, charging door; *c*, opening in shaft; *t*, condensing chambers; c, chimney. The hearth extends beyond the breast into a small raised platform, v, situated immediately before it. The lining of the hearth consists of refractory firestone, and the bottom is hollowed out of brasque, *g*, in such a way as to afford a gentle slope from the side of the tuyer to beyond the front wall. A tapping hole, *o*, is provided at the lowest part of this basin, in order to draw off its contents, when accumulated in sufficient quantity, into a pot placed on a level with the floor. The blast is supplied by two tuyers placed side by side. In charging the mineral is thrown to the side of the tuyers, while the fuel is directed towards the breast. The cold air entering through the tuyers chills the slag in the vicinity, and produces round the nozzles cylindrical prolongations 6 or 7 inches in length, on the proper management of which depends in a great measure the success of the operation. One of the principal effects of these nozzles is to prevent the oxidation of the lead; the blast being brought directly to the fuel, without having to pass through the mineral charged at the back of the furnace, cannot so readily give rise to the formation of fusible silicates. The smelter, therefore, directs his attention to the regulation of the length of these nozzles, as by them the economical working of the furnace is materially affected. The supply of air and fuel must also be so proportioned that the upper part of the shaft may not become too strongly heated. The fume is made to pass through several chambers built of brickwork before escaping into the chimney. Doors are provided for removing the lead soot when necessary. The slags flow continuously into the fore-hearth, where they solidify and are removed by means of a stout iron hook, and are dragged down the inclined plane to the floor. When tapping is performed, the product which collects in the pot is readily divided into two parts; the lower portion is metallic lead, the higher consists of sulphide of lead, with other metallic sulphides, but chiefly sulphide of iron. This is called the first *matt*, and as it readily solidifies, it is removed from the surface of the melted lead by an iron eye, round which a circular cake soon forms. From a charge of the composition described above 19 quintals of lead are obtained, and 8 quintals of first matt, containing from 30 to 35 per cent. of lead.

Fig. 11.

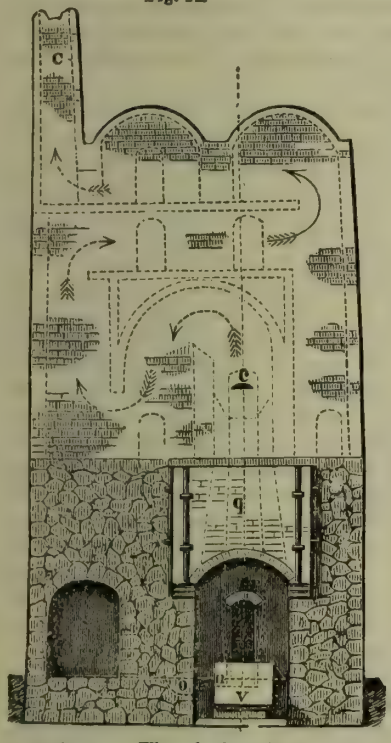
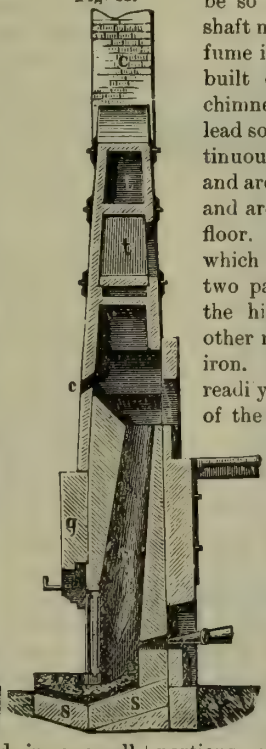


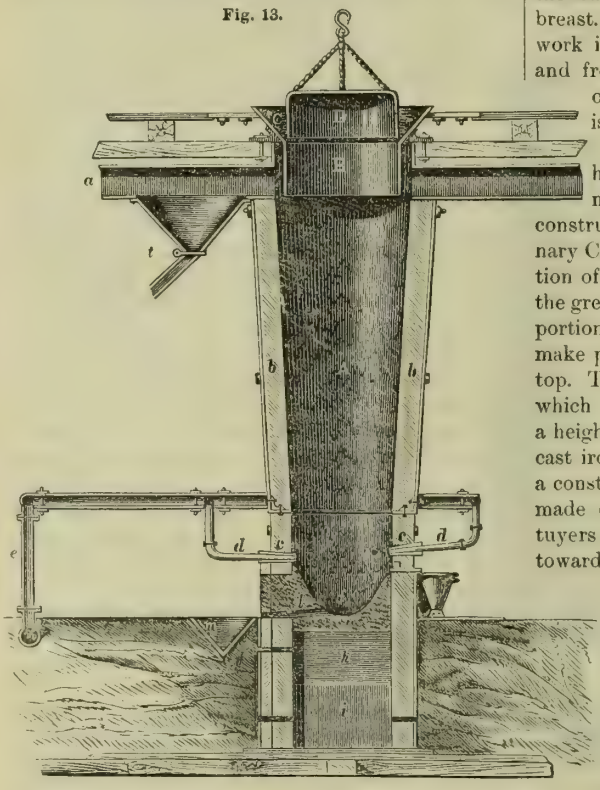
Fig. 12.



When these first matts have accumulated in sufficient quantity they are roasted in open heaps, by which operation a large proportion of the sulphur is removed as sulphurous acid gas. The calcination occupies three or four weeks, and has to be repeated upon such portions of the material as still contain sulphides. For this purpose, at the end of the operation the heap is carefully picked over, and only those parts which have been properly oxidised are taken to a blast furnace of smaller dimensions for reduction. The fuel is coke, and the blast supplied by a single tuyer. Metallic iron is supplied with the charge, and a second matt of sulphides obtained. The second matt is roasted in the same manner as the first, and thus a third and fourth are produced; the last one, becoming rich in copper, is known as the copper matt, and is subsequently treated for coarse copper. Basic silicates of iron, such as refinery cinders, have to a great extent superseded the metallic iron in the smelting works of the Hartz. Still more recently, highly ferriferous copper slags have been employed.

Some other forms of blast furnaces have been tried at various works, with more or less successful results. The Raschette furnace differs essentially from other blast furnaces in its horizontal section, being long and rectangular, and in its having a row of several tuyers on each of its long sides, with a tap hole on each end or narrow side. The hearth bottom slopes downwards towards each narrow end. Water tuyers are employed, generally four or five on each side. The body of the hearth is also kept cool by water blocks. The first trial of the Raschette furnace for lead smelting was made at the Altenau Smelting Works, in the Upper Hartz, and it was afterwards introduced at Ems, Stolberg, Saalfeld, Mansfeld, and Fahlun. After the first experiments

Fig. 13.



at Mühlheim on the Rhine, it has not been successful in Germany. The Pilze furnace is externally of cylindrical form, wider at the top than the bottom, with circular or octagonal section inside, and supplied with from five to eight tuyers, somewhat on the principal of Sefström's assay furnace. The Pilze blast furnace is represented on Fig. 13; A, furnace shaft; B, cylinder with funnel top, C; D, bell for charging by raising it up; *a*, tubes for gas; *b*, *b*, fire-brick surrounded with iron plates; *c*, *c*, water tuyers; *d*, *d*, nozzles; *e*, blast-pipe; *f*, hearth made of brasque, *h*, fire-clay; *i*, slag bottom; *l*, tap-hole, in three troughs or pots for lead and matt; *m*, slag vessel; *t*, funnel with sliding plate for removal of lead soot. The furnace is covered with iron plates, and is furnished with a funnel and charging cylinder at the top, similar to the iron blast furnaces. The height of the shaft is 6·27 métres, with 1·45 métre diameter below, and 2·35 métres above. At Freiberg the Pilze furnace has been lately modified with advantage, the shaft being more cylindrical. The walls round the hearth are cooled with water, or, as in the Upper Hartz example, by air channels. At Pise, near Alais, the fire-stones at the level of the tuyers have been replaced by iron walls cooled with water. Before blowing in the furnace the plates inside are covered with a layer of gypsum, upon which is plastered a layer of slag; by this means a campaign of two to three months is accomplished without repairs. The Pilze furnace is worked in Nevada with a pipe or canal from the deepest part of the hearth, by which the lead continually flows into a pot in front of the breast. A regular flow of lead with more convenient work is thus obtained. The product is more pure, and free from iron and zinc, whilst the formation of masses of iron at the bottom of the furnace is avoided.

The blast furnace now employed at Couëron has been described by Phillips in his "Elements of Metallurgy," and is of a very improved construction. It is considerably higher than the ordinary Castilian furnace. It is employed for the reduction of the roasted siliceous ore of that district, and the grey slags from the reverberatory furnace. A proportion of agglomerated lead-fume and iron slags also make part of the charge. The furnace is fed at the top. The brickwork of the lower part of the furnace, which ordinarily burns away quickly, is replaced to a height of about 3 feet by an annular cylinder of cast iron, kept cool by the circulation through it of a constant stream of water. This cast-iron body is made of one piece, and has five holes for as many tuyers equidistant from each other, and converging towards the vertical axis of the furnace. In this furnace as much as 25 to 30 tons of stuff are smelted in twenty-four hours, the slags being reduced at the same time to a yield of one half to a quarter per cent. of lead. A smelting campaign lasts three months without interruption. Generally four or five tappings, each of 16 to 20 pigs, are made every shift of twelve hours. The consumption of gas coke of inferior quality is 10 per cent. of the furnace charge. No iron is added, and no matt is obtained. The slags are sometimes so highly basic that it is necessary to add sand to the mixture, in order to render them sufficiently fusible, and to prevent the furnace from gobbing. The most fusible slags contain about 30 per cent. of silica. The loss of lead, exclusive of fume collected in the flues, is 6 per cent.

Condensation of Lead Smoke.—Besides a large volume of sulphurous acid gas which issues from the chimneys of lead smelting works, the smoke is white with lead fume, and many have been the inventions to condense this valuable ingredient. The fume in a fine state of division is maintained for a long time in a state of suspension in a perfectly still atmosphere, notwithstanding its great density. It

deposits very slowly, and flues of great length, as well as chambers of considerable capacity, are required for the purpose. Jets of steam and water have been both applied to facilitate the settling of the fume; and these methods have the advantage at least of condensing to some extent the sulphurous acid, which is quite if not more hurtful to vegetation than the lead smoke itself. Another method consists in forcing the smoke, by means of pumps or fans, through water. In Derbyshire and Cumberland the system of long horizontal flues prevails, varying from 2000 to 4000 yards long, and terminating in a vertical chimney of sufficient height to establish a proper draught. In 1843 Stagg patented a method of forcing the smoke through water, which was applied at the Nent Head Works at Alston Moor, and at the Dee Bank Works near Holywell. The pumps are worked by an 800 horse-power engine. The apparatus is subject to great corrosion from the sulphurous acid. The oscillation of the water from the action of the pumps is prevented by packing the chambers with brushwood to the level of the water. It has been noticed that the water which flows from these condensers is more charged with lead soot during the first period of calcination of the ore in the reverberatory furnace than at any other period; an indication that it is at this stage of the process that the greatest loss by volatilization takes place. At Keld Head, in Wensleydale, Stokoe's condenser is in use. This consists of two rectangular chambers, each divided into eighteen compartments. The bottom of each chamber is covered with water, and water falls constantly from the top in the form of rain. Two floors formed of open joists divide the chamber horizontally, upon which fagots are laid. The smoke is forced by a fan successively through the eighteen compartments; whilst meeting with the descending jets of water, the fume is washed off the fagots, so that the filtering apparatus does not get obstructed.

At the Eggleston Mill, near Alston, the smoke from the furnaces passes into the lower part of an arched flue, and upwards through a layer of large pebbles, resting on a bed formed of rectangular pieces of stone set at a proper distance apart from each other. The smoke in passing through the layer of pebbles meets with water, which is dashed down upon the bed intermittently from a series of troughs or buckets suspended on trunnions at their ends. The troughs tilt over as soon as filled, and are thus self-acting.

Some curious facts have been recorded regarding the deposition of lead smoke; and the fact that it is more readily arrested upon dry materials has been proved by filtering it through porous coke, and by the observation that in flues near the furnace containing 2 or 3 feet of stagnant water scarcely any fume deposits.

The lead soot itself consists mainly of lead sulphate, and may yield by assay as much as 60 per cent. of metallic lead. It varies in colour from grey to white, and it has been sometimes ground up with oil for paint.

Refining.—The lead produced from ore in reverberatory furnaces is sometimes so free from impurities that it may be at once used for most technical purposes. It is usually submitted to an operation called poling, which consists in holding a log of green wood beneath the surface of the molten metal, by which means the small proportions of sulphur, antimony, zinc, and copper are separated and removed by skimming. When, however, the metal contains silver to the extent of even 1 oz. in the ton, it is economized, and the lead is submitted to the process of desilverization, either by Pattinson's method or by zinc, in a manner afterwards to be described. The hard lead produced from smelting slags and poor ores in the blast furnace must be softened or calcined to remove the foreign substances it contains. The simplest operation is that mentioned above as carried out at the Alport Works, and called kettling. The hard lead is thrown on the highest part of the bed of the reverberatory furnace and allowed to liquate, whereby the more easily fusible lead leaves a mass containing most of the sulphur, antimony, iron, and copper. If this operation be carefully conducted, the amount of impurities left in the lead will not reach more than 1 per cent. Spanish lead, containing a larger quantity of antimony, is softened by oxidation in reverberatory furnaces at a higher temperature. The operation can be carried out on a slag bottom, but is now usually performed in a furnace which has a cast-iron rectangular pan for its bed. The charge of pig lead may consist of from 10 to 20 tons. After melting, or rather liquation, the more infusible matters are removed by means of a shallow skimmer, perforated with holes, and the heat is then got up until the mixed oxides of lead and antimony are melted. When the slag thus formed is very liquid, it is sometimes thickened with lime to facilitate its removal. In this operation the antimony is oxidised along with a quantity of lead, and is thus concentrated in the lead which is obtained by re-smelting the dross, until, upon repetition of the calcination, the slags finally yield an alloy of lead and antimony, which may be used by the type founders. Richardson gives the following analytical results from these operations:—

ENGLISH HARD LEAD.

	I. Original Lead.	II. Lead from Dross of 1st Calcination.	III. Lead from Dross of 2nd Calcination.
Lead,	99·27	86·53	52·84
Antimony,	0·57	11·29	47·16
Copper,	0·12	traces	traces
Iron,	0·04	0·34	traces

SPANISH HARD LEAD.

	I. Original Lead.	II. Lead from Dross of 1st Calcination.	III. Lead from Dross of 2nd Calcination.
Lead,	95·81	64·98	56·60
Antimony,	3·66	29·84	43·40
Copper,	0·32	5·90	traces
Iron,	0·21	0·29	traces

The iron pans used in the calcining furnace are made with rounded corners to prevent cracking, and in some cases are provided with movable side plates which can be replaced as they are worn through by

the corrosion of the melted oxides, thus saving the permanent sides of the pan. This action takes place chiefly at the level of the liquid charge, the metal beneath the level being practically unacted upon for years. PHILLIPS describes an improving furnace of this kind in use at Pontgibaud in which a charge of 20 tons is softened in 60 hours. The pan is tapped by means of a conical hole in the bottom which is kept plugged by an iron bar. Formerly the improving pans were lined with fire bricks at these works in order to protect the iron from corrosion, but it is found that when the furnace is not overheated, so as to avoid fusion of the dross, the lining is unnecessary. Calcination at a dull red heat, with the addition of a little lime from time to time, are the conditions required for successful softening and for preservation of the furnace.

The softened lead obtained by the treatment of calcination now contains only traces of sulphur, iron, and antimony, but silver and copper remain in proportions which render further operations necessary. The silver must be removed on account of its intrinsic value, and, as will be described subsequently, on account of its imparting a pink tint to white lead. Copper is objectionable also when the lead is to be converted into red lead for use in the manufacture of flint glass.

Pattinson's Desilverizing Process.—This admirable process was discovered by HUGH LEE PATTINSON, at Alston, in Cumberland, and was described by him in a paper to the British Association in 1838. The patent entitled "An Improved Method of Separating Silver from Lead" is dated October 28, 1833. The process depends on the fact that pure lead crystallizes at a temperature above that of lead alloyed with a certain proportion of silver, so that if a pot of melted lead be gradually cooled down and carefully stirred all the time, the contents will soon separate into a mass of crystals which may be fished out with a perforated ladle, and a liquid portion which contains much the larger proportion of silver. By repeating the operation enriched lead containing from 400 to 600 ozs. per ton is obtained, whilst the poor lead is brought down to 10 dwts. per ton.

The operation is usually conducted in a series of from 9 to 12 cast-iron pots, which if worked by hand contain 6 tons of metal each, but when cranes are employed for working the ladle 10-ton pots are more generally used: they are ordinarily 5 feet 4 inches in diameter and 2 feet 6 inches deep. A pot at one end of the series has a capacity of only two-thirds of each of the others, and is known as the *market-pot*.

Each pot is provided with a separate fireplace, and is heated by a circular flue passing round it, which can be closed when required by means of a damper. This communicates with a main flue under the level of the floor parallel with the line of pots. Supposing the lead operated upon to contain about 21 ozs. of silver per ton. If the market pot be called No. 1, the lead will be introduced into No. 6; when melted it is carefully skimmed from dross, and the fire at once withdrawn. Cooling is now promoted by sprinkling water on the surface, and while the temperature is thus lowered the lead is kept constantly stirred with a chisel-pointed bar called a *slice*. The portions which solidify and adhere to the sides of the pot are removed, and thrust under the surface of the liquid metal, when they again become melted. By this treatment crystals soon begin to make their appearance, and the labour of stirring increases. A large perforated ladle is now used to bring out the crystals; the contents are well shaken, and allowed to drain into the pot whence they have been removed, and then are transferred to the adjacent pot No. 5, in the direction of the market pot. This is continued until two-thirds of the lead in pot No. 6 has been taken out in the form of crystals, whilst the lead remaining in No. 6 is ladled into No. 7, and will contain about 40 ozs. of silver per ton. The crystals transferred to No. 5 will yield about 11 ozs. per ton. A fresh charge of lead being worked in No. 6, the crystals are again passed to No. 5, and the enriched *bottoms* to No. 7. Each pot as it becomes filled by crystals from the one side, or by bottoms from the other, is in its turn crystallized. In this way the crystals as they approach the market pot become gradually poorer in silver, whilst the pot bottoms passing in the contrary direction increase in richness. Any lead that may be on hand assaying about 40 ozs. of silver will be introduced into pot No. 7, while lead containing 11 ozs. will be melted in No. 5. The other pots in the series may in the same way from time to time receive lead yielding the same amount, or a nearly similar amount, of silver per ton as the metal which they severally contain. When this system, which is known as the method of *thirds*, is strictly adhered to, the lead in each pot will be approximately twice as rich in silver as that which is next to it in the direction of the market pot. If, however, a different lead has been introduced into any of the pots, the ratio of this progressive increase in silver may be more or less interfered with. In the richer pots the separation of silver is less complete than in the poorer ones, and consequently the progressive enrichment will not be so rapid. In working the last pot of enriched lead the whole of the bottom is not always ladled out, as it is found advantageous to subject it to the following treatment. When the ordinary quantity of two-thirds of the lead has been transferred in the form of crystals to the pot next to it, the remaining one-third will consist of a mixture of crystallized and fluid alloy. The latter being much richer than the former, and amounting to a little more than one-half, is separated by pressing the mixture with the curved side of the large perforated ladle, when the still liquid alloy enters the bowl, and is removed by a smaller ordinary ladle. The lead thus obtained will evidently be richer in silver than the portion remaining in the kettle in the form of crystals.

During these operations a quantity of oxide is produced, and when the charge in each pot is melted down it is always carefully skimmed before cooling. The amount of dross from working lead containing 20 ozs. per ton may be estimated at 25 per cent. of its weight. The ladle employed for hand work is

16 inches diameter, 5 inches in depth, and is pierced with half inch holes. When cranes are used the ladles are 20 inches diameter and 62 inches deep, with three-quarter inch holes. The thickness of the iron is half inch, and length of handle 9 feet 6 inches. When the ladle gets chilled during the operation of crystallizing, it is heated to the proper temperature by being placed for a minute or two into the pot of hot lead in to which the crystals are turned over. Formerly small pots, called heaters or *temper pots*, were used for this purpose, and were placed in the angle formed by the junction of the larger pots.

Although the method of thirds is that usually adopted for the desilverization of lead moderately rich in silver, no general rule can be laid down with regard to the system of working to be employed, as this must be more or less varied in accordance with the particular requirements of the case. For the desilverization of poor argentiferous lead a system called the method by eighths is sometimes employed, when, instead of removing two-thirds of the contents of each pot in the form of crystals, seven-eighths are taken out in that state. The treatment of poor argentiferous lead may, however, be effected by a combination of the two systems, beginning by the method of eighths; the enriched lead may be further concentrated by the method of thirds. The proper conduct of PATTINSON'S process depends much upon the attention of the workmen to the management of the fires and to draining the crystals; and must be checked by constant assays of the results of each operation.

Some modifications have been introduced in order to facilitate the stirring and separation of crystals. WORSLEY invented a mechanical stirrer, which was employed for a short time at the Rotherhithe Lead Works, and a similar plan, known as the *système Laveissière*, was tried at Rouen and elsewhere, but has been abandoned.

Pattinsonizing by Steam.—The process of crystallizing by steam was first introduced at the lead works of Messrs. LUCE and ROZAN at Marseilles, and has been described by ROZAN in a paper contributed to the *Berg und Hüttenmännische Zeitung* in 1874. Instead of mechanical or machine stirring during the crystallization, steam is forced into the melted lead, and produces a similar movement to that which is obtained by the boiling of a dense liquid. The continual agitation produced has been found in practice extremely favourable to the formation of crystals poor in silver, and consequent separation of enriched fluid lead. The action of the steam is essentially a mechanical one. No chemical action has been observed, so that the operation must be preceded by the usual treatment by oxidation at a red heat for impure lead; moderately hard lead can be worked at once. The oxides which are formed at the commencement of the operation are yellowish, but towards the end they are dark coloured and cupriferous, a circumstance which does not occur in the ordinary PATTINSON'S process, however well the stirring is accomplished. At the end of each crystallization, while the steam is still agitating the fluid portion in which copper, antimony, and arsenic have concentrated along with the silver, it is observed that the copper is separated in the dross. Antimony is removed by the oxidizing action of the air at each successive remelting. It is noticeable that soft lead yields a greater quantity of oxide than the hard antimonial lead, a proof that this metal in the presence of lead oxidises first, and to a certain extent protects it from oxidation. ROZAN states that both time and labour are saved, since 13 to 16 tons of lead can be crystallized in less time than 9 to 10 tons by the old process.

The separation by the new process can be always carried out by the method of thirds. The apparatus

Fig. 14.

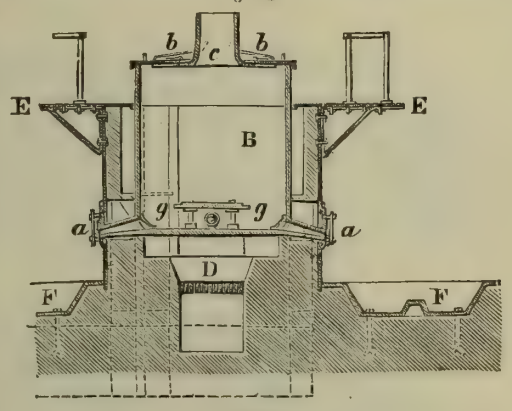
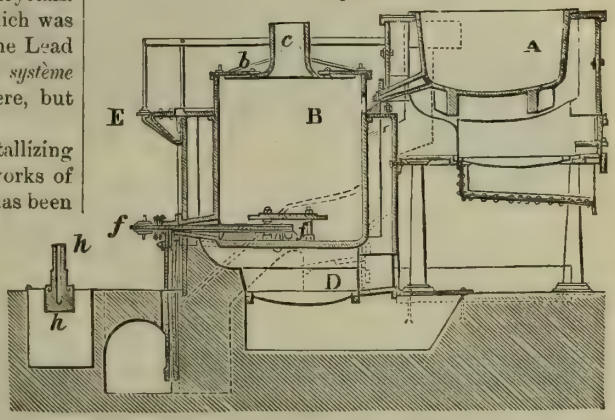


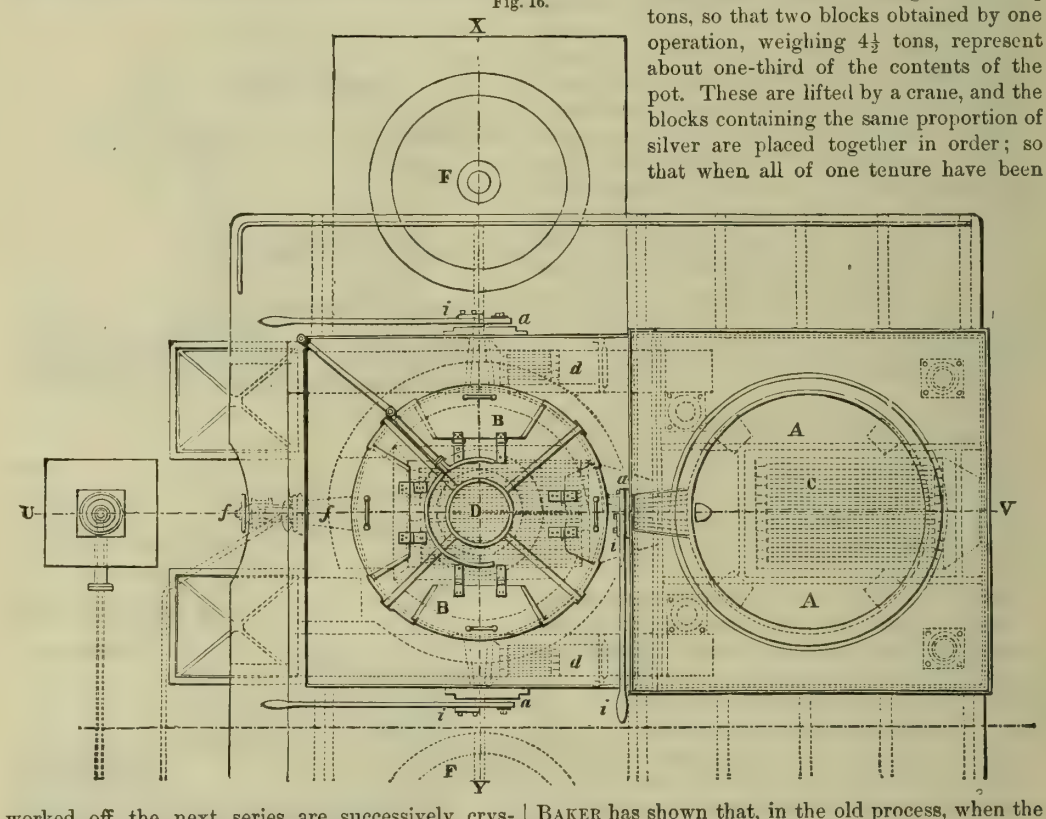
Fig. 15.



(of which Fig. 16 is a plan; Fig. 15 a section, U—V, Fig. 16; Fig. 14 a section, X—Y, Fig. 16) consists of two pots placed at different levels; the upper one, A, receives the lead to be melted for the operation, and holds 9 to 10 tons, the lower one, B, in which the crystallization is carried out, contains 15 to 16 tons. A platform, E, nearly level with the rim of the lower pot, enables the workmen to remove the dross, and to watch the progress of the crystallization. Iron pipes, furnished with friction plates, *a*, *a*, for closing them, are attached to the pots for the purpose of tapping off the lead. In order to prevent the lead running into the steam pipes they are pro-

vided with valves. The work-lead in the upper pot having been well melted and skimmed is tapped off into the lower vessel, and a small current of steam is turned on to promote the mixing of the crystals left in the pot from the last crystallization. A gentle stream of water on the surface of the lead at the commencement is useful for cooling, and for the formation of crystals. The steam at a pressure of three atmospheres is introduced by a pipe at the side, and the current is opposed and broken up by a cast-iron plate, *g*, *g*, which is placed horizontally over the stream. The pot is covered by an iron cover, *b*, *b*, made in segments, which can be removed in turns by the workman as occasion requires, and admits of the removal of the portions which solidify at the sides above the surface of the charge. Two small fire places, *d*, *d*, which are filled with fresh fuel immediately before tapping off the lead, are placed to heat the pipes through which the lead flows out. The vessel, B, is furnished with a tapping pipe on each side. The workman removes the oxide at once before the steam is fully turned on. The segmented cover has in the middle a small chimney, *c*, which communicates with a condensing chamber, where the oxides carried forward by the current of steam settle in the form of a mud. The charge is tapped off when about two-thirds of the lead has formed into crystals. The rich lead is then run into round troughs, F, sunk in the floor. The tapping pipes are provided with strainers to keep back the crystals.

Fig. 16.



Each block thus cast weighs about 2¼ tons, so that two blocks obtained by one operation, weighing 4½ tons, represent about one-third of the contents of the pot. These are lifted by a crane, and the blocks containing the same proportion of silver are placed together in order; so that when all of one tenure have been worked off the next series are successively crystallized. When the lead is sufficiently enriched, or when the market lead has to be tapped into moulds, it is accomplished by the tapping pipe, *f*, under which is placed a ladle on a radial arm, which allows of its being moved round over the moulds placed in a half circle beneath. ROZAN makes the following comparison of cost, and loss of lead and silver:—

	Cost per Ton.	Loss of Lead.	Loss of Silver.
Pattinson's hand process,	46·54 francs.	3 per cent.	1·5
Pattinson's steam process,	25·82 "	2·1 "	1·5

The steam process has now been in successful operation at several of the English lead works, and the fact of the removal of copper to a greater extent than by the hand process has been well established. BAKER has shown that, in the old process, when the proportion of copper does not exceed ·025 per cent., it is found to follow the silver; and lead with such a tenure may be refined for the purpose of making glassmaker's red lead. When, however, the copper reaches about ·05 per cent, six or seven crystallizations fail to reduce it below ·04 per cent. Nickel, also, in the proportions found in Derbyshire lead, viz., ·002 to ·005 per cent., is found to become concentrated in the fluid portion.

Parke's Process.—Desilverizing by means of zinc was the invention of ALEXANDER PARKES of Birmingham in 1850, and was carried out at the works of SIMS, WILLYAMS, & Co., at Llanelly, in 1859. It is remarkable, that both at these works and at Friedrichshütte, near Tarnowitz (where the process was

investigated by KARSTEN and LANGE), it was abandoned on account of practical difficulties, which have now been overcome. But it was not until 1866 that the operation was again attempted at the works at Commern and at Call. When lead and zinc are melted together, and then allowed to cool, an alloy of zinc and lead is formed which solidifies on the surface, and which contains also the greater part of the silver. The fluid part of the charge will contain about half a per cent. to 1 per cent. of zinc, which has to be removed by oxidation in a softening furnace or otherwise. The subsequent treatment of the zinc-lead alloy was performed by liquation in an inclined iron retort, heated somewhere above the melting point of lead. This operation produced lead with about 10 ozs. of silver per ton and left a more infusible alloy, having a composition of nearly one-half lead and one-half zinc, with the greater part of the silver. The zinc alloy was then distilled with a little lime and coal-dust, in clay retorts, on the Belgian plan, to recover the zinc, leaving in the retort metallic lead and pulverulent matter. The lead was remelted and cupelled for the silver, the residual matter scraped out of the retort, and smelted with the ordinary charges of the lead furnace.

Such was the process as originally devised and carried out by the inventor. The treatment of the argentiferous zinc alloy and the removal of the zinc from the desilverized lead afforded scope for a number of plans, which have been put in practice with more or less success. The most effective methods now in use are the addition of the zinc to the charge in three successive portions—cooling and skimming after each mixing; the softening of the lead by oxidation of the zinc in an improving furnace; and the smelting of the argentiferous zinc after liquation in a small blast furnace, with the admixture of lead slag and tap cinder, the lead thus obtained being fit for cupellation.

For the complete desilverization of argentiferous lead, the following proportions of zinc have been found necessary:—Lead containing 250 grams. of silver per 1000 kilos. requires 1¼ per cent. of zinc; lead containing 4000 grams. requires 2 per cent. of zinc. One of the best methods of carrying out the zinc process is as follows:—At a height of about 8 feet from the level of the floor three cast-iron pots are placed in brickwork over separate fire-places; the largest of these has a capacity of about 12 tons of lead, while the other two are much smaller, and contain about 3 tons of metal. The lead to be desilverized is melted in the larger pot, where the usual quantity of zinc is added in three successive portions, and the argentiferous alloy removed to one of the smaller pots. In this pot a portion of the associated lead is separated by liquation, and the zinc alloy is taken out by shallow perforated ladles. When one of the smaller pots has become filled with skimmings it is carefully liquated, whilst the other pot serves in the meantime for the reception of skimmings from the larger pot. The lead eliquated in the smaller pots, containing a considerable proportion of zinc, is added to the next charge of original lead. That remaining in the large pot after removal of the third zinciferous skimmings is tapped into the pan of an improving furnace (Figs. 17 and 18; *a*, cast-iron pan; *b*, working door; *c*, tap-hole; *k*, pot for melting very impure lead, which after removal of dross is run into the pan by the channel, *d*), situated at a lower level, where it is kept at a full red heat during about twelve hours, and is occasionally skimmed with an iron rake. At the expiration of this time it is drawn off into a cast-iron pot, and ladled into moulds as market lead.

Fig. 17.

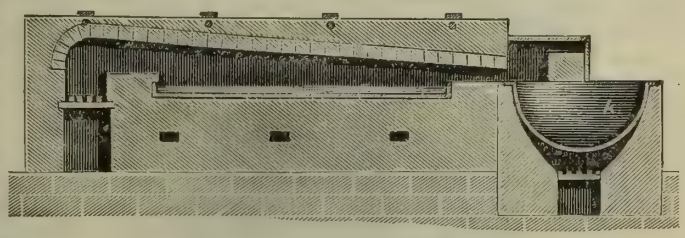
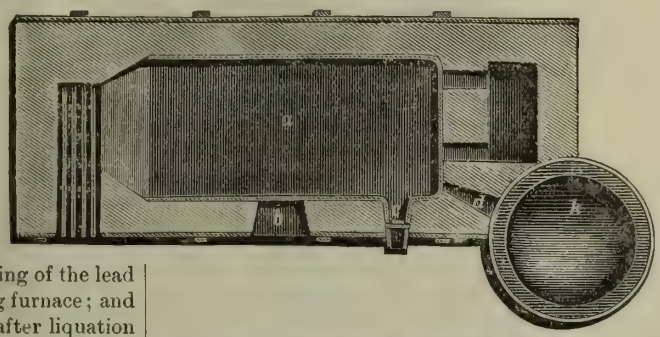


Fig. 18.

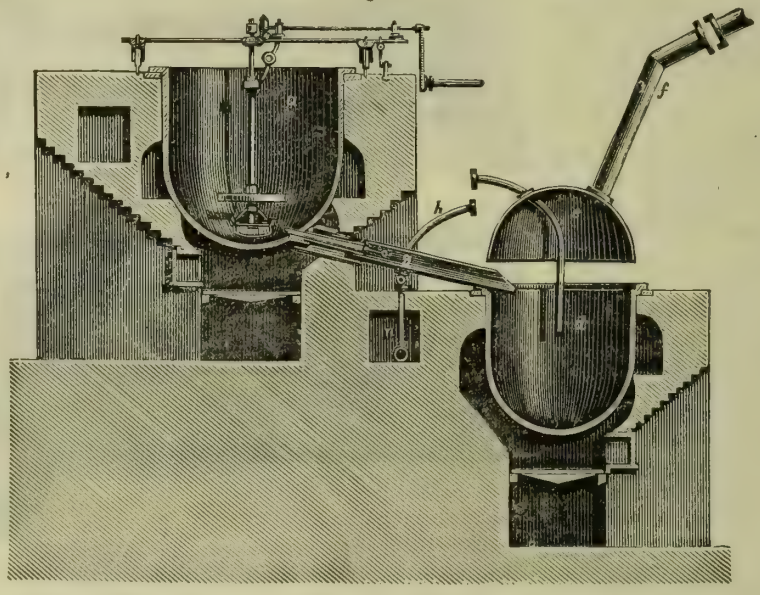


At some works it was thought necessary to sink the portions of zinc to the bottom of the pot, by inclosing them in a box furnished with holes; and to effect a more thorough mixing by a machine for stirring the charge, moved by hand. There is, however, not the slightest difficulty in mixing zinc with lead, provided the proper temperature be attained.

At Call, in Prussia, plumbic chloride, obtained by treating the lead fume from the flues with hydrochloric acid, was used to effect the removal of the zinc from the poor lead. For this purpose the lead was melted at a moderate heat under a layer of the lead chloride, when by frequent stirring zinc chloride was formed and lead reduced. At the Lead Works in Commern common salt has been employed, whilst at Clausthal the natural potassium salts found at Stassfurt were used. ILLIG proposed to effect the removal of zinc by passing the lead through a small blast furnace, with the addition of sand and tap cinder. The last method is included in a patent obtained by FLACH in 1866 for a method of carrying

out the zinc process, in which it is difficult to discover any novelty. CORDURIÉ has patented the application of superheated steam, which readily oxidises iron, nickel, and zinc, but only slightly acts upon copper, antimony, bismuth, and lead. As zinc alloys first with copper and what traces of gold may be present, and afterwards takes up silver, the use of steam seems appropriate to the removal of the zinc, although it leaves antimony behind. KERL states that in the Upper Hartz the steam process yielded 97·024 per cent. of lead, against 96·86 per cent. obtained by the use of the Stassfurt salt. The following is a description of CORDURIÉ'S process applied to the desilverizing operation :—The zinc is either melted in the bath of lead and stirred with iron paddles, or placed in an iron box (Fig. 19), and plunged to the bottom of the fluid metal in the pot, *a*, so that the melted zinc rises in divided streams, and is mixed by means of a shaft to which the box is attached, and with which it is caused to rotate by turning the crank handle, which is geared to the shaft by toothed wheels. After the stirring apparatus is taken out and the zinc alloy removed, the desilverized lead is tapped into a gutter, *g*, which conducts it into the pot, *d*, where it is submitted to a current of steam, which is introduced by a pipe, *h*, passing through a movable dome-shaped cover, *e*, which is furnished with another pipe, *f*, to conduct the steam away. The cover also protects the workman from the injurious vapours arising from the operation. The steam is superheated by passing through the flue, *n*, and is applied to the melted lead when it is at a low red heat. When a sample shows that the zinc has been completely removed, and the cooled surface exhibits the crystalline character of antimonial lead *(antimonspiegel)*, the steam is allowed to pass through the metal for a short time longer to avoid explosions;

Fig. 19.



the cover is removed, and the lead skimmed. Afterwards air is admitted with the steam, until the antimony is oxidised and the iridescent colours peculiar to softened lead appear. The following are analyses of two samples of lead treated in this manner at the works in the Upper Hartz :—

Copper,	0·0014	....	0·0020
Antimony,	0·0056	....	0·0033
Iron,	0·0022	....	0·0912
Zinc,	0·0083	....	0·0007
Silver,	0·0004	....	0·0007
Bismuth,	0·0054	....	0·0036
Nickel,	0·0006	....	0·0007

GRUNER in 1868 published an account of CORDURIÉ'S process as carried on at Messrs. ROTHSCHILD'S works at Havre, and predicted that it would shortly supersede other methods. PERCY is of a contrary opinion, and at present it has not been adopted in England.

Koch's Lead Desilverizing Apparatus.—At Clausthal an ingenious apparatus arranged by HERR ERNEST KOCH was tried in 1873, and described by the inventor in a communication to the *Berg und Hüttenmännische Zeitung*, which gives an admirable account of the conditions required for the economical working of the zinc process.

1. *Separation of Copper by Liquation.*—The original lead is first liquated in a furnace, which differs only slightly from the ordinary reverberatory furnace. The fire-place is at *c*, Figs. 20, 21, and 22; the products of combustion pass from *b* to *a*, and escape to the chimney; the floor of the furnace slopes from *a* to *d*, so that *a* is the highest and *d* its lowest part; the molten lead flows into the pot, B; the residue is moved by means of a paddle from *a* towards *b*, where the highest temperature prevails, thoroughly liquated by stirring, and finally raked out. The furnace is kept in continuous working. As fast as lead runs

into the pot, fresh pigs are thrown in, and the more infusible residue removed, the heat being so regulated that the gases only escape at a temperature below the melting point of lead. The length of the furnace, or the distance between *a* and *b*, must be arranged for certain dimensions of the fire-place in order to obtain this result. The liquated residue will contain the chief proportion of the copper originally present in the lead. The melting points of copper and lead differ considerably, so that the more carefully the liquation is carried out the more complete is the separation of these two metals.

The pot, B, serves for the collection of the needful quantity of lead for further treatment. After filling it is tapped into the pot, C, except a small quantity, which is left as a reserve in case of irregular working of the liquation furnace charges, as well as to provide a covering of oxide for the lead flowing into it from the furnace. As a protection from cooling this pot is provided with an iron cover.

2. *Removal of Antimony.*—After the lead in the pot, C, has reached red heat, steam is passed through the charge, and the crusts of oxide (*abstrich*) removed. The oxide of antimony strongly corrodes the iron vessel, so that in time it becomes eaten through; and this pot should be cast with a thicker rim. Oxidation of the antimony is much promoted by exposing a large surface to the action of the air by frequent stirring, and by a shallow form of pot. Antimony hinders the formation of the zinc-silver alloy, keeping the latter metal in the fluid portion when much antimony is in the lead; it is therefore essential to

Fig. 20.

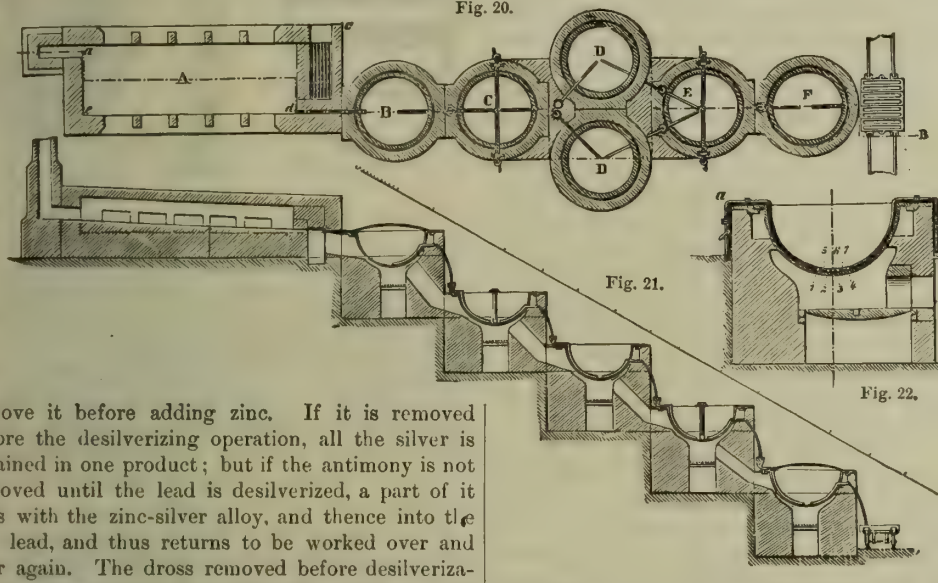


Fig. 21.

Fig. 22.

remove it before adding zinc. If it is removed before the desilverizing operation, all the silver is obtained in one product; but if the antimony is not removed until the lead is desilverized, a part of it goes with the zinc-silver alloy, and thence into the rich lead, and thus returns to be worked over and over again. The dross removed before desilverization contains some lead mechanically mixed up with it. It is stamped to a fine powder, whereby the lead shots are flattened and most recovered by passing through a sieve.

3. *Desilverizing.*—The lead deprived of antimony is now tapped into the desilverizing pots, D, D, by means of a syphon, having one leg a foot longer than the other, which delivers the metal into a funnel attached to the side of the pot below, and is the upper part of a wrought-iron pipe terminating at the bottom of the pot. The funnel is filled with coke, and the lead flows into it from the upper vessel, and thence to the lower pot, without suffering oxidation. During this operation the appropriate quantity of zinc is placed at the bottom of the pot, in front of the opening of the iron pipe, so that the zinc is immediately brought into contact with the silver contained in the lead. The charge is now stirred, cooled, and the zinc alloy skimmed off in the usual way. As this operation is repeated three times, it is necessary to have two desilverizing pots, in order that a continuous working of the apparatus may go on. Upon mixing the lead and zinc two distinct alloys are formed—silver-zinc alloy and lead-zinc alloy. These are separated, not so much in consequence of their different specific gravities, as by the difference of their melting points. The silver-zinc alloy solidifies first in the process of cooling, and afterwards as the temperature falls the lead-zinc alloy crystallizes out. The formation of the first alloy may be promoted by exposing a larger surface for cooling, either by gentle stirring by hand or by a current of steam; in the latter case the silver-zinc crystals are readily detached from the sides of the pot, and brought to the surface in the form of a pasty scum. As the formation of a rich silver alloy and a poor lead alloy require opposite conditions, the former being promoted by a minimum of zinc, the latter by an excess, the following operations can be divided accordingly into the production of a rich zinc-silver alloy and a poor zinc-lead alloy.

The rich zinc-silver alloy is formed by making use of the alloy produced by the third addition of zinc to the former charge to the new charge of lead, and is effected by placing it at the mouth of the pipe through which the hot lead, free from antimony, is flowing into the pot. The thorough mixing is accomplished by steam, and the first zinc alloy

taken off is now rich enough to be set aside. An experiment of this operation when the lead contained 0·16 per cent. of silver after the first hour's skimming, proved its reduction to 0·3 in five hours, whilst the zinc alloy contained from 0·74 to 0·94 per cent.

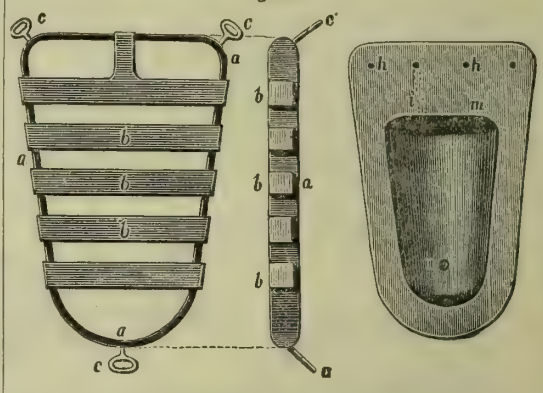
The formation of the poor zinc-lead alloy is accomplished in a similar manner by the addition of fresh zinc only at the third operation.

4. *Separation of Zinc from the Poor Lead.*—The desilverized lead is now tapped into pot, E, and when the metal is red hot steam is passed through and air excluded. The steam is decomposed and the free oxygen forms oxide of zinc. This decomposition is more readily effected when the steam is in finely divided streams, issuing from several orifices, 1, 2, 3, &c., in the pipes *a* and *b*, Fig. 22. The oxides are skimmed off, the metal tapped into the pot, F, where it is cooled, and cast into moulds, except a portion which is left to preserve the pot at a uniform temperature, and to afford a covering of oxide for the next charge. It is advisable to provide the pot, F, with a cover, to avoid loss of heat and oxidation. All four operations can be effected in the same time, so that as soon as one pot is empty the next charge is also ready to be operated upon, the working being continuously carried on. As combustion of the fuel is never complete under a single pot, in the system of pots here described arrangements are made for the products from the fire under the pot, F, to pass to the space under E, and so on up to the liquation furnace, by which means also better economy of fuel is effected. The use of gas from an ordinary generator furnace would be still more advantageous. Much of the value of this apparatus depends upon the method of tapping the metal from one pot to the other. This has been usually done by means of a pipe from the bottom of the pot; but when heated to a high temperature such pipes are apt to fracture. This difficulty has been met by Koch's plan of syphons which pass out at the side of the pot about $1\frac{1}{2}$ feet above the bottom. Although the arrangement of a satisfactory syphon, and the proper thickness of the vessel at the point where it passes out, offered considerable difficulties in practice; it has been found possible to work them, and to tap off 12,500 kilos. of lead in three minutes without loss.

Cupellation.—The enriched lead obtained by either Pattinson's or Parke's process has now to be submitted to the operation of cupellation, which consists in oxidising the lead in a suitable furnace, at a heat in which litharge melts; a blast of air is directed on to the surface of the charge so as to constantly uncover the face of the fluid metal, and expose a fresh surface to oxidation.

The hearth of the furnace is composed of bone ash, and forms the movable bottom of a reverberatory furnace. The cupel or *test* is contained in a oval iron ring, *a* (Fig. 23), about 6 inches in deptn, and 4 feet in its greater, and 3 feet in its lesser diameter. This frame is provided with cross bars, *b*, *b*, *b*, $4\frac{1}{2}$ inches wide, and half an inch in thickness, and handles, *c*. The *test-ring* is most frequently made of wrought-iron bars held together with rivets, but in some cases it is formed of cast iron, and is then cast in one piece, including the bars across the bottom. When the test is prepared it is filled with bone ash, well beaten down in layers, after having been slightly moistened with water containing a little pearl ash in solution, to

Fig. 23.



give firmness to the cupel when heated. The centre is carefully scooped out with a small trowel until the sides are left 2 inches at the top and 3 inches at the bottom, whilst the thickness of the sole itself is about $1\frac{1}{4}$ inch. At the front or wide end, *m*, of the test the bone-ash border is allowed to stand for a width of 6 inches, and is furnished with holes, *h*, *h*, for running off the litharge, by means of channels, *i*; and an opening, *n*, is cut through the bottom, which communicates by a channel with the fluid litharge in the annular cavity, allowing the fused oxide of lead to run off as fast as it is produced.

When the test is thoroughly dried and ready for use, it is placed in the refining furnace, of which it forms the bottom. Figs. 24 and 25 represent the refinery most commonly employed; *f* is the fire door; *d*, pot for melting the work lead; *e*, chimney; *g*, hood for carrying off the fume; *l*, nozzle of blast-pipe; *t*, bed of furnace. The fireplace is nearly square, and may be about 2 feet by 2 feet 4 inches. This is separated from the body of the furnace by a bridge of from 14 to 18 inches in width; the products of combustion pass directly over the surface of the cupel, and escape by two separate apertures into the main flue. The test is strongly wedged into an iron ring built in the masonry of the furnace. When first lighted great care is necessary to regulate the heat, to prevent the bone-ash cupel from cracking. When properly annealed and brought up to dull redness, the rich lead is ladled on to the test from an adjacent iron pot, *d*, in which it has been previously melted, and which is provided with a fireplace and a gutter to conduct the lead on to the test. At first the metal becomes covered with a grey dross, which melts down when the temperature of the bath increases. The blast is now turned on, and the fused litharge is driven from the back of the test up towards the breast, where it passes over the broad edge of bone ash and falls through an aperture

between it and the iron frame of the cupel, and is received in a small shallow cast-iron pot running on wheels, and provided with a long handle.

In some works the lead is introduced in the form of pigs, instead of being run on to the test in a fluid state. The blast, which is usually supplied by a fan, but sometimes by a steam jet, sweeps the oxide along the surface of the metal towards the breast, and at the same time supplies the oxygen necessary for the formation of litharge. As the metallic bath diminishes fresh lead is added, until the charge becomes so much enriched that it is ready for tapping. When lead from the rich pot contains about 600 ozs. of silver per ton, the cupellation lasts eight hours, during which time 32 cwts. of metal will have been introduced into the cupel, and 6 cwts. of enriched

Fig. 24.

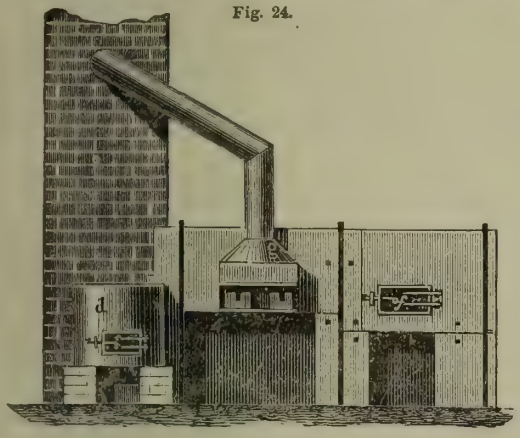
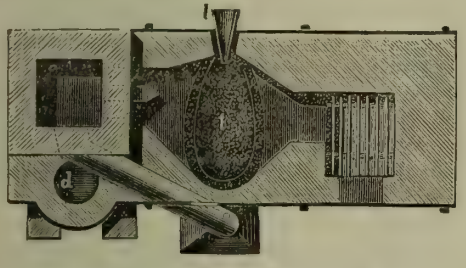


Fig. 25.



alloy remain. This argentiferous lead is tapped by drilling a hole in the bone ash forming the bottom of the cupel, and running it off into a pot on wheels. The tap-hole is then closed with a plug of wet bone ash, and another charge introduced into the furnace. When all the lead has been thus treated, the argentiferous alloy is operated upon in a similar manner; but now the last traces of lead are oxidised, and the *brightening* (*blicken*, *éclair*) of the silver indicates the termination of the process. The blast is turned off, the fire removed from the grate, and the plate of silver allowed to set. At a certain stage of cooling the cake of silver, which originally presented a smooth mirror-like surface, is roughened by the evolution of oxygen which had been absorbed during the operation. A refinery of the usual dimensions will work off 4 cwts. of lead per hour, and consume about 6 cwts. of coal per ton of lead. The cake of silver may contain from 2 to 3 per cent. only of other metals.

On the Continent some of the lead obtained from the smelting furnace is frequently rich enough to be treated in the cupellation furnace without previous concentration. The old German cupelling furnace consists of a kind of reverberatory oven, having a circular hearth and a fireplace at the side. The bottom is regularly hollowed out from the sides towards the middle, and is composed of firebricks closely set on edge, upon a solid stratum of firmly compressed slag. This is covered with a coating of marl carefully beaten down with iron rammers, and is relaid previously to the commencement of a fresh operation. The layer of marl is the equivalent to the bone-ash test employed by English refiners. A dome of iron plastered over with marl covers the bed, and may be removed by means of a crane. There are five openings in the side of the furnace; the largest admits the flame from the fireplace; two smaller ones are for the tuyers, by which the blast is thrown on to the fused metal, forcing the litharge as it forms towards another opening, by which it escapes in a fused state. The fifth opening is for the introduction of the lead. As the level of the metallic bath lowers, a *gate* is cut in the marl by means of a serrated iron bar, to allow the litharge to flow out on to the floor of the building. About 5 tons of ordinary lead are cupelled at one operation, and of this about three-fourths are introduced into the furnace before lighting up; the rest is added at intervals during the progress of the cupellation. The pigs of lead, which are hemispherical, are placed with the convex side downward, so as not to injure the marl bottom. On the centre of the heap billets of wood are placed and lighted by a shovel full of charcoal; the iron dome is dropped into its place, and luted round with fire clay. The blast is then turned on, and a fire of billets made on the grate. No chimney is provided. After three to five hours the charge is melted, and the scum (*abzug*) is removed by skimming or raking it off towards the channel made for the litharge. Afterwards the metallic bath becomes bright and clear, and acquires a gentle circular movement; it is, however, quickly covered with pasty and impure litharge (*abstrich*), which is likewise removed until the pure litharge begins to flow. The brightening of the silver generally takes place in thirty to thirty-three hours after turning on the blast. Towards the close of the operation the temperature must be considerably increased to keep the argentiferous alloy in a liquid state. The plate of silver (*blicksilber*) thus obtained contains a little lead and copper, &c., and is removed from the furnace to be refined either in a movable test, like that employed in the English process, or in a fixed cupel forming the bottom of a reverberatory furnace. The litharge formed in the process of cupellation is treated according to its quality in the following ways. The impure litharge is resmelted, as well as a large proportion of the purer kind, when there is little demand for flake litharge, whilst the litharge obtained

at the end of the cupellation is of necessity reduced to the metallic state again, in order to economize the silver it contains.

The reduction is easily effected in a reverberatory furnace with a bed sloping towards the tap-hole in the usual way. The litharge is thrown on with an admixture of bituminous coal, a layer of slack having been previously spread over the bed of the furnace. The skimmings and dross from Pattinson's process can be likewise worked up at the same time. At Clausthal the litharge is reduced in a blast furnace 20 feet high, lined at the bottom with coke stones, made of finely powdered coke mixed with clay instead of the ordinary bricks, which in consequence of their siliceous nature too readily formed a fusible slag with the oxide of lead.

The following analyses of market lead are quoted from W. Hampe of Clausthal, who worked upon 400 grammes for each analysis, in order to obtain accurate estimations of the impurities:—

Locality.	Copper.	Antimony.	Iron.	Zinc.	Silver.	Bismuth	Nickel
Hartz.....	·0014	·0056	·0022	·0008	·0004	·0054	·0006
Villach.....	·0021	·0052	0025	·0032	trace.	—	—
Tarnowitz,.....	·0013	·0022	·0080	·0080	·0015	—	—
Bleiberg,.....	·0014	0037	·0016	·0016	0008	—	—
Newcastle,.....	·0526	0074	·0015	·0018	·0040	—	—
London,.....	·0758	·0032	·0022	·0032	·0020	—	—
"	·0094	·0021	·0016	·0010	·0007	—	—
Mechernich,....	·0024	0018	·0009	—	—	—	·0007
Stolberg,.....	·0018	·0024	·0006	—	·0010	·0036	·0009

The chief uses of lead in the arts are for building purposes, in the form of sheets for roofs, gutters, and spouts, pipes for gas and water, shot, and for making solders. In chemical factories lead lined vats are frequently required, and the large chambers of the sulphuric acid factories are made of the purest lead autogenously soldered.

Sheet Lead is made by first casting a large square or rectangular plate several inches in thickness, and then passing it through a powerful pair of rolls fitted with reversing gear. The lead should be cast at a temperature which just allows of skimming off the dross which arises without the lead sticking to the tools. The sheet may be either rolled whilst still hot, or as practised at some mills may be rolled cold. The rolls, which are about 18 inches in diameter, are placed at the middle of a long bench or frame about 3 feet high and 8 feet in width. At intervals of every foot are placed wooden rollers parallel with the cylinders, and all on the same level; these facilitate the movement of the sheet as it passes through the mill. In rolling lead the ends of the sheet present a concavity, which shows that the metal near the surfaces extends more than the central portion, which is contrary to what occurs in rolling iron. The lead passes backwards and forwards through the rolls from 200 to 300 times, and when the length of the sheet becomes inconvenient to manipulate, it is cut into two and each piece milled separately.

The lead for pipes is sometimes mixed with a little harder lead, containing tin or antimony, in order to stiffen the pipes, make them brighter, and to enable the plumber better to preserve the round form in making joints.

In the ordinary way of making pipes a short thick cylinder is first cast, which is then reduced in diameter and elongated, by being drawn on a mandril of the proper size through a succession of steel dies. By this method lengths of from 20 to 30 feet only can be obtained. When longer pipes are required without joint, a machine worked by a hydraulic press is employed. The lead is melted in a cylindrical reservoir placed over the piston of the press, and surrounded by an annular fire-place. At the top is fitted a steel die of the diameter of the outside of the pipe to be made, whilst a mandril passes directly through the centre, and is moved upwards by the rising piston at the same time that the semi-molten lead is forced through the die. A spout through the top of the reservoir enables the workman to fill it with lead; it is then removed, and the aperture firmly stopped by an iron plug secured by a strong key. As the pipe escapes at the top it is coiled round a drum, and may be made of any required length.

Lead Shot is made by mixing a certain proportion of white arsenic or arsenical dross from the improving furnace with molten lead, and allowing it to run through cullenders pierced with holes of a suitable size, and to fall a considerable height into a receptacle containing water. The admixture of the arsenic imparts fluidity and a tendency to coalesce into spherical drops in passing through the air, as well as hardness in the finished article. About 3 lbs. of white arsenic or orpiment are used to 1000 parts of soft lead, and about 8 lbs. for the harder kinds. R. Smith in Percy's laboratory found in a sample of No. 1 shot, 0·133 per cent. of arsenic acid and 0·030 per cent. of copper. A sample of No. 6 contained 0·115 per cent. of arsenic and 0·284 per cent. of copper. The arsenical alloy is ladled by the workman into the cullenders, which are lined inside by the dross being pressed down and against the sides, so that the metal does not run too fast, a regular flow producing more equality in the size of the grains.

Three cullenders are generally used at the same time, and are kept hot by being surrounded with a charcoal fire. The height from which the lead falls is determined by the size of the shot required. A fall of 33 yards is required for No. 4 to No. 9, whilst for larger sizes 50 yards may be used. The size of the holes in the cullenders varies according to the size of the shot which is to be made; but must always be smaller in diameter, perfectly round, and free from burrs. The temperature of the lead bath is also regulated by the size of the shot. For the largest it should be such that a bit of straw plunged into it will be scarcely browned.

The shot when taken out of the tub are sorted by sieving into the different sizes, and the imperfect spheroids separated, by placing them on a board about 27 inches long and 16 inches broad, inclined very slightly, so that when gently shaken in the horizontal direction the globular particles run down

and bound off into a suitable box, whilst the irregular forms remain on the sides of the tray.

The shot, which have now a light grey colour, are placed in a small octagonal cask mounted on a horizontal axis, and polished by attrition with a little black lead.

White Lead—*Céruse, Blanc de Plomb; Bleiweiss.*—When lead is exposed to the action of air and moisture it becomes converted into a white mass of plumbic carbonate and hydrate. This corrosion is facilitated by the presence of acetic acid vapours; and the white lead of commerce, which is the chief basis of all the pigments, is made by artificially submitting the metal to oxidation in an atmosphere loaded with carbonic acid gas and steam in the presence of acetic acid. The oldest or Dutch method of effecting the change into white lead was to bury coils of lead, which were placed in earthen pots containing a little weak vinegar, beneath layers of stable litter, and after the lapse of a few weeks the pots were taken out and emptied of their contents of more or less corroded lead, from which the white lead was detached from the metallic part left uncorroded by beating or stamping; it was then washed and ground to a fine powder. Upon this method was founded the English process, by which nearly all the white lead is made in this country at the present time. In the early part of this century the horse litter and the sour ale or "alegar" were replaced by the spent bark of the tanners and pyroligneous acid, or the impure acetic acid obtained by the distillation of wood. By this means the discoloration often produced by the hydric sulphide evolved in the fermentation of the horse litter was avoided; at the same time greater regularity in the process was obtained. The operation is carried on in brick chambers, called "stacks," which are made of various dimensions, according to the judgment of the manufacturer. Some prefer an area of 20 feet by 12 feet, others build them double this size. Experience, however, has proved, that with the smaller stacks it is quite as usual to get a high percentage corroded as with the larger ones. The stacks are conveniently built in two rows, leaving a sufficiently wide passage between them for the carriage of bark, timber, and materials used in filling them. Each stack has an opening in the front wall from top to bottom, about 3 or 4 feet in width. In some cases a similar opening is made in the back wall, so that the stack may be loaded at one opening and the materials removed at the other, when the time arrives for taking off the white lead. The floor of the stack is covered with a layer of porous ashes, and upon this is thrown a bed of spent tan which has been previously allowed to reach a somewhat active stage of fermentation. When in good order the tan going on to the stacks has a pleasant lemon-like odour. It is usual to mix the old tan coming off the stacks with the tan which is received from the tanners, and to stack it up in the yard under cover, or even in the stack-way against the walls of the stacks, and to leave it for use when the proper stage of fermentation is attained. Much of the success of the process depends upon the state of the tan; and it is probable that regular working could be much more surely obtained if correct data were kept of the amount of moisture and the average temperature, as well as of the weight and bulk of bark used. Upon this first bed or "height" of tan are placed blocks of wood cut from larch trees, of about 16 inches diameter, to support wooden bearers about 4 inches square, which in their turn carry boards which cover the bed like the floor of a room. Upon the tan earthen pots are placed quite close together over the whole bed, except a space of about 6 inches left round the walls. The tan under the blocks is beaten down, so as to give a firmer support to the superincumbent weight; and the general surface of the bed is made slightly convex to resist the pressure above, which acts more upon the centre than the sides. The pots are nearly filled with dilute acetic acid, containing about 0·5 to 0·75 per cent. of pure acetic acid, $H_2(C_2H_2O_2)$; and upon the pots are placed piles of metallic lead cast in various shapes, and called crates, buckles, crosses, plates, &c., according to their form. The layer of lead will be about 5 inches, and an interval of about 6 or 8 inches is left between the lead and the covering of boards to allow of them sinking without coming into contact with the white lead, as well as to permit of the increase in bulk of the latter. The interval between the pots and the side walls is filled up by placing a board edgewise against the pots, and filling in with straw or tan. The stack mouth is also filled in with tan, which is kept up by boards placed in slots or against the inside of the opening; and this tan, which is generally old tan, is kept uniformly pressed, so as to admit air very gradually. The next beds are prepared in the same manner, only that the blocks may be of less diameter, and the beds of tan made of diminishing thickness at each successive height. Ten or sometimes twelve beds are thus stacked, and the top covered over with its layer of bark. As fermentation proceeds the whole system of beds gradually sinks; and it is usual to visit the top of the stacks at intervals, and to stamp down the bark which falls away from the side walls, and thus to check the issue of steam, which now escapes freely from the heated tan. The temperature attained is sometimes 140° Fahr. In some works wooden spouts are used, which traverse the beds from top to bottom, and are placed either at the corners of the stack, or one may be fixed in the middle. These wooden ventilators are pierced with holes, and can be choked when necessary by a wisp of straw, or by filling them up with tan. The object sought to be attained by this arrangement is to allow of a quantity of steam to escape at the first active period of fermentation, so as to avoid a large amount of condensation, which, carrying with it the colouring matter in the tan, would discolour the white lead as the drops fell from the covering of boards above.

Experience has shown that in the stacks of large area these ventilators are of advantage, but in the smaller ones sufficient escape and regularity of ascent of the current of vapours is accomplished generally at the surface of the side walls. It is, however,

easy to observe that the character of the corrosions in the centre is generally harder and more dense than those at the side walls, where more moisture has been present. In some cases where the white lead is produced with great excess of aqueous vapour, the corrosions are quite sugary in appearance, crumbling between the fingers into small crystalline grains, which upon analysis are found to be nearly pure neutral plumbic carbonate, $PbCO_3$. The bulk of the white lead produced is a mixture of carbonate and hydrate, generally represented by $2PbCO_3$, PbH_2O_2, or $3PbCO_3$, PbH_2O_2, but on the same bed proportions varying from these may be found. A very small quantity of plumbic acetate is also locked up in certain, if not all, kinds of corrosion, as may be proved by treating a large quantity of the pulverized corrosion with water. Moreover, in the manufacturing operations of grinding and levigating—subsequently to be described—the water, if used over and over again, becomes charged with the soluble salt of lead. The best corrosions are hard, and almost porcellanous in fracture, and if the lead used is of pure quality they are of a fine opaque whiteness. Sometimes they present a floury character, which gives rise to a good deal of waste on removal, by crumbling under the touch, and which produces a large quantity of froth on the water of the becks when grinding. A slight discoloration is sometimes observed on the surface of the white lead corrosion from tarry matter in the acid used, and still more from the dropping of water coloured by the tan. Such discoloured white lead is usually put aside until sufficient has accumulated to be ground up to supply the potters to make their glazes.

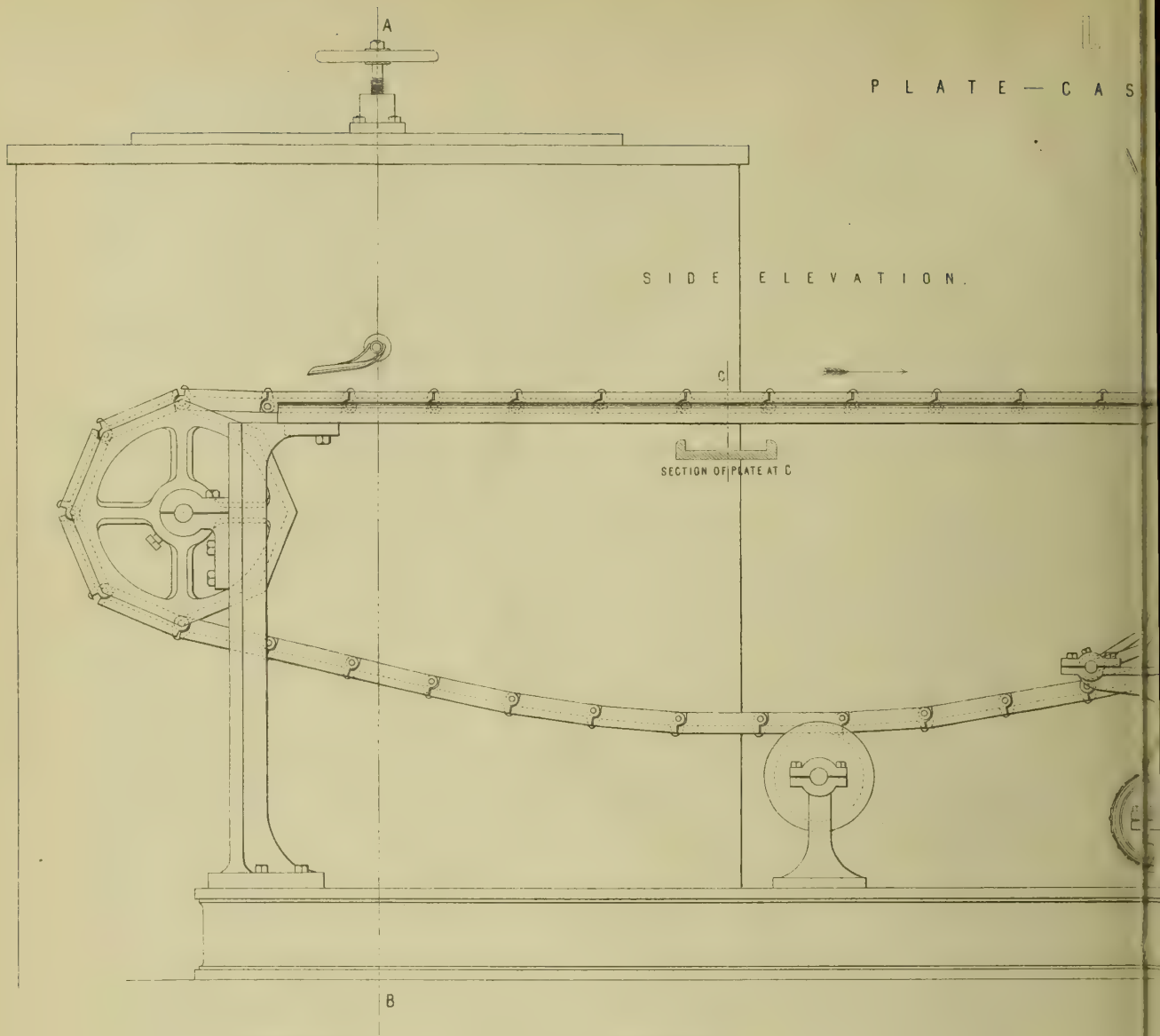
The quantity of lead put on to a stack of 20 feet by 12 feet in area is 3 tons per bed; this quantity will lie upon about a thousand pots of 5½ inches diameter, containing 200 gallons of weak acid. The percentage of lead corroded varies from 50 to 70 per cent.; but perhaps the average result may be stated at 65, and the increase in weight, allowing for unavoidable waste by fine particles falling into the bark, may be reckoned at 20 per cent. of the lead employed.

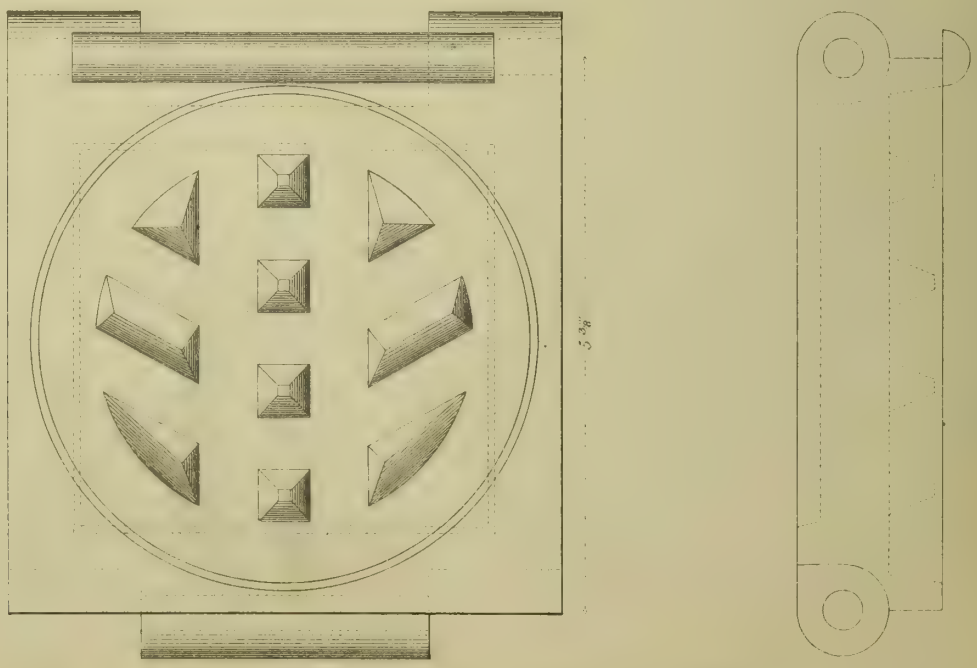
Most of the white lead works purify their own lead, either by Pattinson's or the zinc process. The influence of small quantities of impurities in impairing the whiteness of the product is very remarkable, and the purest lead is essential. On reference to the table of analyses it will be seen that iron is seldom in any appreciable quantity in refined lead, and no objectionable colour can be ascribed to its presence in the qualities usually employed. Copper and antimony impart a dull grey tint in the hard corrosions, and the former may be often traced in the softer ones by the blue and green tints which are characteristic. A colour which has been defined as red or pink for a long time was a source of trouble to white lead makers, and has been attributed to defective working causing the formation of an oxide, or to some impurity in the lead. In the whitest corrosion this tint may be frequently detected just at the junction of the metallic core and the white lead. Baker, who once attributed this tint to the presence of copper, has proved that it is due to metallic silver in a finely divided state. In 1868 a large quantity of lead was decopperized by means of zinc, at the Sheffield Lead Works, leaving a quantity of silver which varied from 15 dwts. to 1 oz. of silver per ton. About 80 tons of this lead were placed in the stacks for corrosion, when the whole of it came down of a uniform pink tint. This lead only contained a trace of copper or other substances. Subsequently synthetical experiments were made, by adding minute quantities of silver to pure lead which had already produced white corrosion; on submitting them to the process in the stacks the samples furnished the pink coloured carbonate. The alloying of zinc with lead removes copper very completely before silver, and seems to leave the silver so thoroughly dissolved in the melted state as to bring out the colour very clearly; for it was found, that the addition of antimony in small quantities, by producing an alloy less soluble in melted lead, was effective in masking the pink tint.

The lead is cast in the desired form by ladling into frames containing the moulds mounted on a horizontal axis, which allows of the plate being turned over and brought smartly against a bar of iron, so as to throw the castings on to the floor. The lead should be only heated moderately, so that the crates do not show any of the oxidation colours when set. Freedom from traces of antimony is shown by the whiteness of the castings, whilst a small quantity will be at once disclosed by the iridescent colours which appear even at a low temperature. An excellent machine for casting the plates or buckles is shown in Plate I., and has been introduced at the principal lead works in this country and in America. It consists of an endless band of square plates of iron linked together, each plate being a mould, into which the lead is poured when brought under the spout of the lead pot. The spout terminates in a sort of trough or gutter, perforated with two or three holes at the proper distance, to deliver a little stream of lead and feed the mould equally. The machine is speeded to make 50 plates per minute, but is worked to 62 or 64 without difficulty. The castings are delivered at the end on a leather belt, covered with plates of sheet iron to prevent the hot buckles injuring the leather, and are thus carried away from the machine.

When the stacks have been up from eight to nine weeks they are unloaded. The oldest bark from the top covering and mouldy portions are carried out of the way; the rest is mixed with new bark, and stacked or carried on to the bed being put up. The corrosions with the portions of metallic lead are placed in trays; the larger pieces fallen on the bark also picked up by hand; the surface of the bed raked, and carried away to be washed to recover the white lead particles it contains. The pots, which are generally dry, except a few which contain water produced by condensation of the steam evolved during the process, are washed and drained for use in the next bed going on. The trays of corrosions

PLATE — CAS

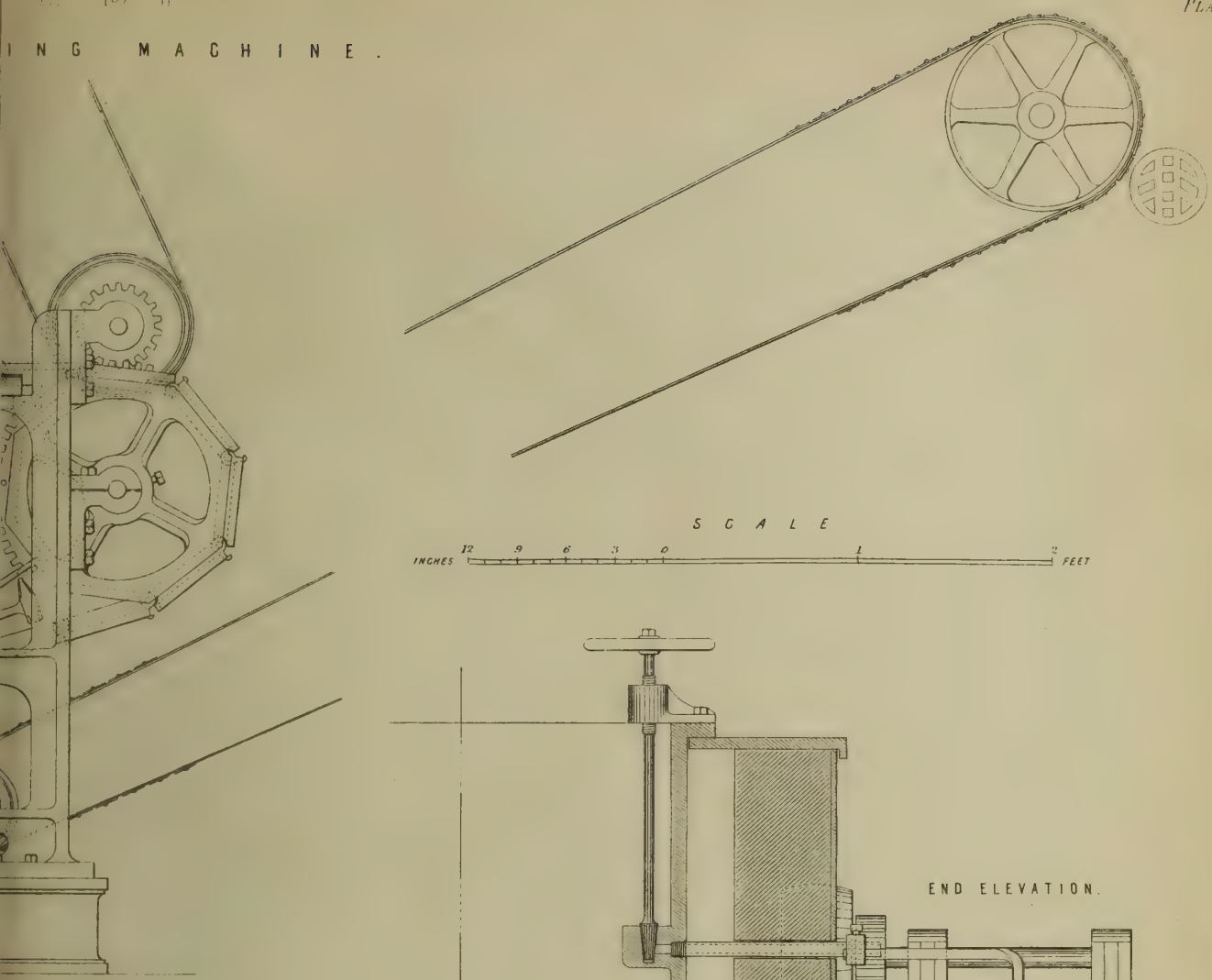




ENLARGED PLAN & SECTION OF MOULD.

J. E. LIPPINC

ING MACHINE.



SCALE

INCHES 12 9 6 3 0 1 2 FEET

SECTION OF KETTLE & FURNACE THROUGH A B

END ELEVATION.

are carried to the mill for grinding and levigation. This operation is accomplished in a variety of ways at the different works. The best method is undoubtedly to sink the tray into a cistern of water, and detach the metallic part by means of rakes or other tools, which direct them between corrugated rollers running under a stream of water. To empty the tray of dry corrosions in front of the rolls without a complete soaking in water is dangerous, on account of the poisonous dust it produces. When the metallic parts are thus separated, the white lead is further crushed by passing through a pair of smooth rolls, and is then raked about over a perforated plate, upon which streams of water fall in the form of rain. The coarse white lead thus produced is carried to horizontal grinding stones, which are fed by means of a ladle, or by an endless band under the guidance of the workman. The white lead now issues like a thick white mud, and may pass through either one or two more pair of stones, until it becomes so fine that the particles are carried away by a stream of water to settle in the becks; the portions which subside in the troughs leading to the settling cisterns are returned to the stones for grinding, and some checks are provided against their being carried forward by means of small strips of wood placed across the channels. Most of the fine particles of bark are removed by the washing, but it is possible to detect in the white lead of commerce traces of the material. The wash water, as was stated above, when it is used over and over again, is always found to contain a soluble salt of lead. This is generally precipitated by the addition of a little sodium carbonate before changing to fresh water. The rolls and machinery which come in contact with the white lead should be made of copper or gun metal. When a cistern is full of white lead the water is turned into another one, and every day as the mud settles down the supernatant water is ladled or syphoned off, until the mud reaches a sufficient consistence for ladling into dishes for drying. The dishes commonly used are shaped like flower-pot saucers, of about 12 inches diameter and 3 inches deep, and are made of the same material. The white lead pulp when placed in the dishes contains about 25 per cent. of water. The dishes are stacked in a drying stove upon shelves made of iron bars; the heat is applied by means of a fire-place outside, the products of combustion passing into large iron pipes which circulate round the floor of the stove. The temperature attained should not rise above 180° Fahr. When dry the white lead is packed into casks, an operation attended with the production of a good deal of dust, which it is difficult to prevent being injurious to the workmen employed. It is now ready to be ground with oil; but if kept for a month before grinding, it yields a better result. The quantity of boiled linseed oil required is from 8 to 9 lbs. per cwt. of dry lead.

The details of the above-described operations may vary at different works. The mode of packing the stacks admits of alterations in the thickness of tan and arrangement of floor boards. Sometimes an interval is left between each board, which is covered by a thinner slab, supported by cross strips of wood, with the object of causing a more general circulation of the air throughout the stacks. The bearers of wood are sometimes laid upon a row of pots, or upon a certain number of larger pots made to contain the crates of lead inside them upon a rim, which separates the lower part containing the acid from the upper part, which is of larger diameter, and furnished with several holes in the side to admit the vapours arising from the tan. Formerly these large pots were the only kind employed; but modern practice restricts their use to the top beds, or simply for those parts of the bed upon which the bearers rest. It is usual when the unscaling operation is completed to weigh the residual metallic lead, and ascertain what quantity has been corroded on each bed. The wet cores, or "returns," are then allowed to dry before re-melting in the casting pan. A notable quantity of white lead is always obtained by washing the bark scraped off the top of the layer under the pots, and in some works the waste bark is burned to diminish its bulk for removal. Wigner and Harland have examined the gases in the white lead stacks (*The Analyst*, September 30, 1876), and find the minimum quantity of air necessary for the work of fermentation and oxidation to be 6 or 7 cubic feet per minute. The carbonic acid varies between 0·5 and 4·5 per cent., but occasionally is found from "traces" up to 27 per cent. At the time of stacking, the atmospheric air included in the stack may be assumed to contain 20·7 per cent. of oxygen; after two weeks it will probably average about 17 per cent., and in five or six weeks may be between 13 and 15 per cent. Occasional samples have yielded only $6\frac{1}{2}$ per cent. No sensible amount of acetic acid could be discovered in the gases.

For ascertaining the composition of white lead it is generally only necessary to determine the plumbic oxide, carbonic dioxide, and the water of combination. Simple ignition at a low red heat in a platinum crucible gives the amount of lead oxide. The carbonic dioxide may be accurately estimated by loss by means of one of the well-known apparatus for decomposing carbonates with acid, and allowing the escaping gas to pass through concentrated sulphuric acid, or a calcium chloride drying tube. The combined water is best estimated by heating the white lead in a hard glass tube in a current of dry air, and collecting the water in a small calcium chloride tube, which is weighed before and after the operation. J. A. Phillips combined the estimations of carbonic dioxide and water by aspirating dry air over the heated white lead, and collecting the water in the calcium chloride tube, and the carbonic dioxide in potash bulbs successively. According to the same chemist, white lead loses its chemically-combined water at 150° C., and its carbonic dioxide towards 170° C. Of course it is necessary, before proceeding with an analysis, to submit the powdered sample to drying in a water oven at 100° C.

The following are analyses of various samples of

white lead contrasted with the theoretical composition of the natural and other carbonates:—

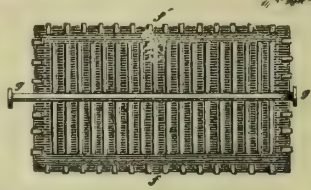
	1.	2.	3.	4.
Plumbic oxide,....	85·95	86·182	85·796	83·537
Carbonic dioxide,..	11·14	10·443	11·259	15·709
Combined water,..	2·91	3·375	2·945	0·754

No. 1. A good dense corrosion, specific gravity 6·322.
No. 2. Dry white lead, London, specific gravity 6·50.
No. 3. " Sheffield, specific gravity 6·14.
No. 4. Crystalline corrosion, transparent and granular.

	Neutral Carbonate, $PbCO_3$.		$2(PbCO_3)$ PbH_2O_2.		$3(PbCO_3)$. PbH_2O_2.
Plumbic oxide,..	83·52	....	86·32	....	85·60
Carbonic dioxide,	16·48	....	11·36	....	12·67
Combined water,	—	....	2·32	....	1·76

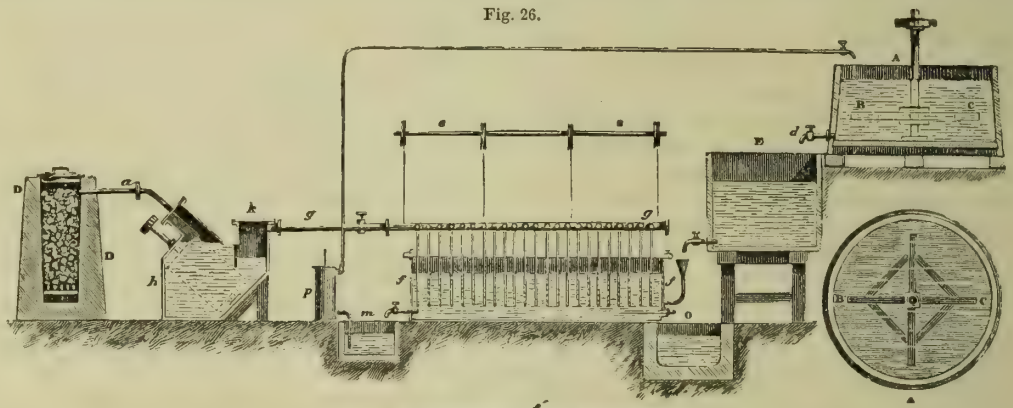
A number of observations proves that the corrosions obtained in the stacks yield upon the average when ground and levigated a dry white lead, which lies between the composition represented by 2 and 3 atoms of the carbonate with 1 of the plumbic hydrate. Wigner and Harland have experimented upon mixtures artificially made up in these proportions, and find that if there is any decided departure from these limits the compound does not afford a useful pigment, its opacity and the power of laying on readily being impaired. These experiments confirm the supposition that there is no definite compound of carbonate and hydrate formed by the action going on in the stacks, but that it varies with the conditions of the fermentation, the volume of carbonic dioxide, and other circumstances. The examination of nearly 1000 samples leads to the opinion that the white lead formed by corrosion in the stacks is not a basic carbonate, but a mixture of a neutral carbonate with a hydrate; and the value of the white lead as a paint, whether it be prepared by the Dutch-English process or by precipitation, depends almost entirely upon the relative proportions of these two different ingredients.

German Process.—Formerly a large quantity of white lead was made at Krems from the pure lead of Bleiberg: the chief place of manufacture is now at Klagenfurt in Carinthia. The operation is carried on in wooden boxes 5 feet long, 12 to 14 inches broad, and 10 or 12 inches deep. The boxes are well jointed, and when nails are used they are carefully covered. The bottom is made tight with melted pitch. Sheets of lead from one-twentieth of an inch to nearly one-half are used according to the fancy of the manufacturer, and these are bent over a square slip of wood, and thus suspended in the wooden boxes. An acid liquor made of about equal parts of vinegar and wine lees is poured on the bottom of the boxes; and they are stacked in a store room, where they are heated to about 85° Fahr. for a space of fourteen or fifteen days. When properly carried on this process yields a weight of corrosion equal to the metallic lead put on; the uncorroded portions being detached and remelted. The carbonate is put into cisterns, and washed and ground for paint in the usual way.



Clichy Process.—When litharge is digested in a solution of plumbic acetate a basic salt is formed, which is quite soluble, and which deposits carbonate of lead upon passing through it a current of carbonic acid gas. This process, established by Thénard, has been carried on successfully in France for a long time. It is said to produce a white lead which has less opacity and covering power than that made by the Dutch process; and this defect has been generally attributed to precipitated carbonates. This appears to be due simply to the much finer state of division of the particles, so that a cwt. of precipitated white lead will take far more oil to make a paint of the usual stiffness, and thus when spread over a surface will necessarily be a thinner film than paint made with white lead whose finest particles are produced by attrition only. The apparatus employed in this process is shown in Fig. 26. A is a tub containing about 4000 gallons of pyroligneous acid, obtained by the distillation of wood. The crude acid is generally redistilled in order to purify it from tarry matters, and should have a specific gravity of 1·056. Litharge is thrown into the tub in the proportion of 174 lbs. to the 65 lbs. of acid, in order to make the basic acetate solution, which should reach a specific gravity of 1·145. The solution is promoted by the agitator, B, C, which is set in motion by machinery. The liquor is then run into a cistern, E, where

Fig. 26.



insoluble matter, such as metallic lead, sulphate of lead, silver chloride, and any other insoluble substances may settle. The clear solution is next run into the vessel, *ff*, in which the precipitation is effected by a current of carbonic acid gas, which is forced through the liquid, and distributed by means of several hundred pipes, having branch pipes at right angles to the main, *g*, *g*, and lying about 13 inches under the surface.

The carbonic acid is generated by a mixture of coke and chalk, but formerly was produced by the combustion of charcoal. Dumas recommended the proportion of 2½ of chalk to 1 of coke. From the kiln, D D, the gas passes into the apparatus, *h*, *k*, in which it is washed, and pumped or blown by a fan into the decomposing vessel. The latter holds about 2000 gallons of liquor from E, which is diluted with water before the operation of blowing in the gas is proceeded with. The passage of the gas lasts from twelve to fourteen hours, when the carbonate formed is allowed to settle; the solution of neutral acetate is drawn off, and pumped up to dissolve more litharge, and supply another charge of basic acetate for decomposition. A certain amount of the neutral acetate is unavoidably lost in these operations, so that it becomes necessary from time to time to add fresh acid. The cover of the decomposing vessel is raised by cords attached to the main pipe, and the white lead is removed by an opening at the bottom leading to the reservoir O, where it is washed repeatedly. The first washings, containing a notable quantity of the neutral acetate, are returned by the pump, *p*, to the tub, A. The white lead is now ready to be dried in stoves in the ordinary manner.

A number of patent processes have been published, but few have been found economical or practicable; and though many are exceedingly ingenious, a description of them rather belongs to the history of white lead inventions. The neutral nitrate has been used instead of the acetate to form the solution of a basic salt, which was precipitated by carbonic acid gas, as in Thénard's process. Granulated lead has been agitated with water in barrels, and exposed to the oxidising action of the air and to carbonic acid at the same time. Benson and Gossage passed carbonic acid over layers of litharge mixed with a small proportion of sugar of lead.

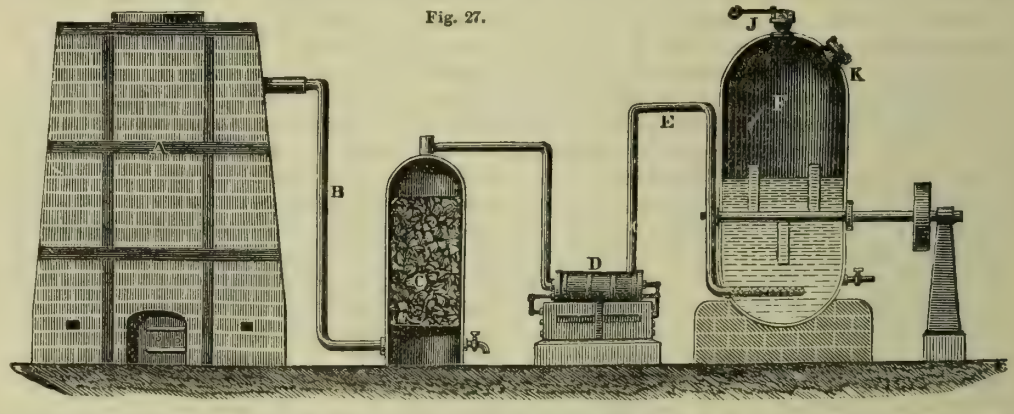
Milner's Process.—At the present time the only process in use besides the Dutch-English manufacture is one founded on the patents of Dale and Milner, and carried on successfully by the Sankey White Lead Company (Limited), near Warrington. The interesting reaction which is the chief part of the invention, depends upon the formation of an oxychloride of lead, made by grinding together litharge, water, and common salt, and may be readily observed on a small scale with a common pestle and mortar. Upon mixing these ingredients together in suitable proportions the mass gradually becomes softer and more pulpy, and admits of a little water being added from time to time as it becomes absorbed, whilst the mass swells up and gradually assumes a white colour, passing through a stage in which it has a pink tint. The great increase in bulk and the softness of the product are very remarkable, and a rise of temperature also takes place. The reaction is now alkaline, the sodium chloride having been decomposed. On the large scale flake litharge is used, which must be carefully ground and levigated. The powdered litharge of commerce is not found so suitable, probably on account of the proportion of metallic grains which it always contains. A mixture in the proportion of 4 lbs. of dry litharge to 1 lb. of salt, dissolved in 16 lbs. of water, is agitated thoroughly in a wooden pug-mill, which is best made of yellow pine, with arms of American elm, and driven by suitable machinery. Oak timber must on no account be used in this vessel. The agitation must be kept up continuously for at least three hours. If the mill be arrested before this time the mass becomes so stiff that it requires removal by hand. Afterwards the mixture again returns to a more fluid condition, and the reaction is complete. The result of this operation is the formation of an insoluble basic chloride of lead, which is suspended in a solution of caustic soda and sodium chloride. The mixture is now run into the carbonating vessel, which consists of an iron cylinder lined with lead, 16 feet high and 8 feet diameter, and fitted with wooden beaters on a horizontal axis, passing through the sides in such a position that the arms of the beaters are alternately above and below the surface of the fluid, so as to obtain as great an amount of agitation as possible. A stream of carbonic acid gas made from chalk and coke in a small kiln, and washed in a coke column supplied with water, is pumped into the vessel, which it enters at the bottom. After the lapse of half an hour or more the solution no longer gives an alkaline reaction; but the current of carbonic acid gas must be continued for some time longer, in order to obtain a pigment having the proper density and covering power. In Milner's last patent, in 1875, he describes a simple test by which the operator can tell when it is necessary to cease the supply of gas.

When the solution no longer shows an alkaline reaction the mixture is a viscid homogeneous mass, and if a portion be tested by shaking it in a glass half filled, it will coat the sides and remain in a uniform layer; but when sufficient gas has been introduced a small quantity shaken in a clear glass vessel will coat the glass with a very thin layer, like frost on a window pane, and after standing a few seconds the clear liquid separates from the carbonate of lead, and leaves an arborescent pattern on the interior of the glass. If, however, the action of the gas is continued for too long a time, the product loses its value, becoming like sand, and will not coat the test glass at all, but settles rapidly out of the salt solution. When the charge in the carbonating vessel has reached the proper stage the contents are run out, and the white lead washed free from the salt solution. This is effected by filtration in the first instance, fresh water being mixed with the pulp when the salt solution has drained away, until it is thoroughly washed. The white lead is then dried in

stoves in the usual manner. The product has the composition of ordinary white lead, and cannot be distinguished from it by chemical analysis, appearance, or by any other properties, as it possesses all the covering power and opacity of the best paint made by the older process. When it is considered that the actual conversion into white lead is accomplished in two days instead of as many months, and that a very simple plant is required, it seems probable that MILNER'S invention will become a successful rival of the long established Dutch method of making white lead. The accompanying Fig. 27 gives a sketch of the arrangement required for carbonating the oxychloride. A is a small kiln for generating carbonic acid gas by the usual mixture of coke and chalk. B is a pipe conducting the gas to the wash tower, C, which is filled with hard coke, over which a gentle stream of water is allowed to flow. If necessary it is easy to wash the gas in a solution of sugar of lead to remove any sulphide of hydrogen it may contain. The gas is then forced by means of a fan or pump, D, into the carbonating vessel, F, which it enters at the bottom, and is distributed by means of a pipe, E, perforated with a number of holes. H indicates a shaft furnished with a drum, which is connected with machinery to turn the paddles or beaters on the axis, L. The liquid is run into the vessel at the opening, K, and does not rise much higher than the horizontal axis of the paddles. J is a valve to regulate the pressure, and M, a tap by which samples can be taken out in order to watch the progress of the operation, and to run off the white lead to the washing cisterns.

Pattinson's Oxychloride of Lead. — A method of making a useful pigment to be used as ordinary white lead was patented by PATTINSON in 1849, and oxychloride of lead is still manufactured by Messrs. BELL & Co. at Newcastle, where its combination with other chemical processes renders it more economical than it would be in localities less devoted to these industries. Chloride of lead is first prepared from finely pulverized galena and concentrated hydrochloric acid, the temperature being raised by a jet of steam. The comminution and solution of the galena is carried on in the same vessel, the bottom of which is formed of a single slab of silicious stone upon

Fig. 27.



which a millstone of the same material moves. The sides of the basin are constructed of bricks capable of resisting the action of acid. The chloride of lead formed during the treatment being little soluble in cold water, and less so in the acid solution, collects at the bottom of the vessel. The acid liquid having been decanted, the deposit is dissolved in hot water, and the hot solution treated with an appropriate quantity of milk of lime, to saturate the free acid and to precipitate any iron which may be present. The liquid is then allowed to settle, crystallization being prevented by the continued application of heat. When clear it is transferred into a large wooden vat into which, at the same time, a stream of lime water is directed in sufficient quantity to precipitate half the quantity of lead. The oxychloride thus formed is collected, drained, washed, and dried on porous earthenware plates in a stove. The composition of the product is represented by the formula $PbCl_2.PbH_2O_2$. The immense quantity of sulphide of hydrogen disengaged during the action of the hydrochloric acid upon the galena proved, in the commencement of this industry, a great embarrassment; the highest chimneys being insufficient to diffuse the gas sufficiently in the atmosphere. Afterwards Messrs. BELL decomposed the sulphide of hydrogen by submitting it to the action of water and of sulphurous acid produced by the combustion of pyrites. In addition to the well-known change—

$$2H_2S + SO_2 = 2H_2O + 3S$$

Another reaction takes place which gives rise to the separation of sulphur, with simultaneous formation of water and pentathionic acid—

$$5H_2S + 5SO_2 = 5S + 4H_2O + H_2S_5O_6.$$

The sulphur is used in the manufacture of sulphuric acid; the pentathionic acid is mixed with magnesia and exposed to the action of the atmosphere, whereby magnesian sulphate is gradually formed.

Several methods of testing the covering power of white lead have been proposed: the simplest is to triturate equal weights of the samples to be compared with equal quantities of linseed oil, and to determine the weight of equal volumes of the pigments thus produced; that which is specifically the heavier of the two will possess the greater covering power. WEISE has examined this property from

the point of view of the chemical composition of the white lead. Having taken the corrosions formed in the chambers by the German process, he examined the products obtained by careful washing and sieving with the following results:—

	Plumbic Oxide.	Carbonic Dioxide.	Water.
No. 1. White lead of the best quality called "flour,"	86·80	11·16	2·00
No. 2. Do. second quality,	86·24	11·68	1·81
No. 3. Do. third quality, still a useful paint,. ..	86·03	12·28	1·68
No. 4. Residue from the washing apparatus,.....	84·69	14·10	0·93
No. 5. Abnormal product from the chambers, quite useless as a paint,. ..	83·47	16·15	0·25

Hardness and want of covering power here go hand in hand, and are caused by the excess of neutral carbonate.

Red Lead, *Minium*, *Triplumbic Tetroxide*, Pb_3O_4. —The manufacture of red lead is often associated with the smelting operations, or may be combined with the processes of refining lead, or the making of white lead, as a large quantity of dross or semi-oxidised products can be conveniently worked up in the red lead ovens. Pig lead is melted at a regulated temperature below that at which litharge melts, and is rabbled about until converted into oxide. The product, when ground and levigated, is a brownish yellow powder, called massicot, and in this state may be dried and packed for sale as powdered litharge. For conversion into red lead the litharge is thrown into a similar oven, and carefully heated, with occasional turning over of the charge, until by the absorption of oxygen the proper colour is reached, and the whole is converted into the brilliant coloured pigment known as red lead.

The ordinary red lead oven is a low-arched furnace, having a bed slightly inclining towards the medium line, and also from the back to the front. The bed is made of closely-laid pressed fire-bricks, and is supported by a bed-plate of cast iron. The plate has raised borders on each side and at the back. There are three openings in front, fitted with hinged doors of cast iron—one on each side for introducing the fuel, and a central larger one, through which the oven is charged with lead, and the charge worked by a rabble. The top of the central doorway is a little higher than the other two, whereby, owing to this slight difference in height, the entrance of air through the side doorways is promoted, as well as the escape of the gaseous products of combustion of the fuel from the upper part of the central doorway. At an equal distance from each side of the oven a low vertical wall, or fire-bridge, extends along the bottom from front to back; and the spaces included between these walls and the adjacent sides of the oven respectively constitute two fire-places, without any grate. The length of the bed from back to front is 11 feet, and the width between the bridges is 8 feet 4 inches. Immediately underneath the middle door is a space, of which the sides are formed of two vertical plates of cast iron, or by narrow brick walls; the back by the lower part of the large cast-iron plate supporting the front of the oven, and containing the central doorway; and the bottom by the floor, which is here covered with a plate of cast iron, or formed of a large slab of stone, the front and the top being left open. This space receives the oxidised lead when it is drawn out of the oven at the end of the first drossing or "dusting" stage. In front of the oven above is an arched space or hood of brickwork, prolonged upwards into a short vertical chimney, and the products of combustion of the fuel and any lead dust carried upwards escape from the oven and ascend through this hood. In front of the central door a chain is suspended, having a hook at the bottom, which serves as a fulcrum for the rabble. The oven is firmly braced by means of cast-iron standards and wrought-iron tie rods. The fuel used in these ovens is coal, in lumps of considerable size; but when they are provided with grates and ash-pits, extending backwards for about one-third of the length of the oven, small coal may be employed. The top of the oven is usually covered with a layer of sand, or other badly-conducting material. At some works the same oven is used for the next operation of colouring as for the drossing. Where a separate oven is employed it differs in a few particulars. There is no cast-iron bed-plate; the bottom is flat, and slopes down 4 inches from back to front. From 22 to 25 cwts. of lead are charged into the oven, and a dam is made across the front with the coarse particles of intermixed lead and oxide resulting from the grinding and levigation of the former charge. This material is beaten down firmly with a piece of flat wood. The lead when melted forms a pool behind the dam, in which the rabble is worked backwards and forwards, each movement splashing the lead over the oxide formed. In about two hours' time the dross which has accumulated is thrust into a heap towards the back of the oven, the pool of lead becoming smaller. At intervals lumps of slag lead are thrown in to assist the oxidation, which it does in a very remarkable manner. The active substance in promoting this oxidation is undoubtedly the antimony contained in the slag lead; and an experiment may easily be made on a small scale, which is extremely instructive. If very pure refined lead is melted in a ladle it will have a smooth white surface, showing little tendency to the display of a succession of oxidation colours; moreover, the surfaces touching the sides of the ladle are convex like mercury. If now a very minute proportion of antimony be added, previously alloyed with lead, so that it will melt at once without raising the temperature, in a moment the surface oxidises, and a succession of colours is produced when the metal is stirred; a quantity of oxide is formed, and the metal licks or wets the surface of the ladle like water. An artificial slag lead can be made by mixing antimony and lead in suitable proportions—about 3 or 4 per cent. of antimony answers the purpose exceedingly well. Baker tried the effect of an artificial slag lead made with sulphur, by melting 2 per cent. of galena with soft lead. The

product was poured out red-hot into moulds, and upon solidifying passed through a pasty condition, like ordinary slag lead or plumbers' solder. Upon breaking the pig of lead thus formed it had a granular fracture, and showed the oxidation colours characteristic of lead free from antimony. When used with an ordinary charge of lead it was found to assist the oxidation, but not so well as the slag lead containing antimony. When red lead is required for glass makers it is important to have it free from copper; therefore if refined lead is used it is necessary to oxidise the lead without the use of the slag lead, or at least to use as little as possible, as it would introduce a small proportion of copper. An experiment was made with the same quality of soft lead with and without the addition of slag lead, and it was found that the drossing was shortened by two hours when slag lead was used. Lead which has passed through the Pattinson process, and is quite free from antimony and sulphur, but containing from 10 to 20 ozs. of copper per ton, was also found to be more readily oxidised than purer lead. This fact must be due to the presence of the copper, although this metal is found to become concentrated during the operation, and a larger proportion is found in the residual lead which remains unoxidised at the end of the shift than existed in the original charge.

The oxidised charge, after it is raked out, is allowed to cool in the space in front of the oven, and is then carried to the mill stones, where it is ground with a regulated supply of water. The heavy particles which sink in the troughs leading to the settling cisterns are used to dam up the charge of lead in the drossing oven. The levigation at some works is performed by receiving the ground stuff from the stones in a puddler in which an upright shaft furnished with arms revolves, whilst a current of water is forced from the bottom and stirs up the litharge, so that the lighter particles are disengaged and float away with the overflowing stream, whilst the heavier green-coloured portions, containing grains of metallic lead, gradually collect at the bottom, and are removed from time to time.

The litharge, when washed and dried, has a brownish-yellow or buff colour, and almost invariably contains a trifling quantity of metallic lead. As powdered litharge is an article of commerce, at this stage it may be simply dried, sieved, and put into casks. For conversion into red lead, the litharge is kept in the oven for forty-eight hours at a regulated heat, whilst the charge is frequently stirred to promote the absorption of oxygen. The progress of the colouring is watched by withdrawing a sample on the paddle from time to time; when hot it has a rich purple tint, and as the conversion approaches completion it assumes the bright colour of red lead when cold.

There is a variety of red lead known as orange lead, which is produced by heating white lead in the colouring oven. At some white lead works, if not at all, occasionally a large quantity of white lead froth is formed during the grinding of very soft corrosions. If this is collected and charged in the ovens, a very soft and bright-coloured orange lead is produced. The different shades of red lead observed in comparing the product of various manufactures, are due chiefly to the amount of carbonate which is formed in the mass of litharge by exposure to the air before it is put into the colouring oven. Lead with much antimony in it will give a lighter colour, from the formation of yellow antimoniate of lead. Red lead when it is drawn from the oven is simply sieved and put into casks. The orange lead must be ground and levigated, as it is submitted to a higher temperature, and the charge is full of lumps from incipient fusion of the litharge.

At some works drossing by machinery is practised by means of a vertical shaft with metal blades, which is fixed in the centre of the oven, the floor of which is oval or disc shaped. The revolution of the shaft keeps the pool of lead in agitation, and as the oxide forms it is heaped around by means of the rabble. It is stated that larger charges can be worked off by this arrangement. The sieving of the red lead is accomplished in a covered apparatus, generally consisting of iron edge rolls, from which the crushed stuff falls into a fine wire sieve working below them, so that the workmen are not exposed to the poisonous dust.

Lead Poisoning.—Efficient ventilation, and cleanliness on the part of the work people, in both white and red lead works, can alone prevent lead sickness. With proper draught in the furnaces, and roomy smelting houses, there does not seem much danger; but in the handling dry white lead corrosions, and packing the red and white lead, it is difficult without intelligence and care on the part of the workmen to avoid poisonous effects of the dust. Lead is introduced into the system through the lungs by inhalation of lead smoke, or air contaminated with plumbiferous dust; through the stomach, by swallowing food or drink impregnated with lead; and through the skin or mucous surfaces, by prolonged contact with lead and its compounds.

The chief symptoms of lead or painter's colic are severe griping pains in the stomach and obstinate constipation. A remarkable and characteristic sign of lead poisoning is a bluish-grey line along the gums at their junction with the teeth. The skin has a dull, dirty, and cadaverous appearance. After several attacks local palsy commonly supervenes. This symptom characterizes the disease called the wrist drop, which is a frequent complaint of the Sheffield file cutters, who use a block of lead to support the file under the blows of the hammer on the chisel. The treatment of a case of lead colic most efficacious appears to be an ounce of castor oil mixed with ten drops of laudanum, to be taken twice daily, and large hot poultices of linseed meal to be applied to the stomach. At night a draught of forty drops of the *liquor opii sedativus* in camphor mixture is prescribed, if the bowels have been acted upon during the day.

In chronic cases potassium iodide has been found to favour the elimination of the poison by the kidneys. It is given in doses of from 5 to 10 grains twice or

thrice daily. Perhaps the most insidious form in which lead is introduced into the system, is by drinking water contaminated with this metal. Soft water, unless deprived of oxygen, which it naturally contains, has an active solvent action upon lead. The contents of an open cistern receiving rain water will be found charged with lead, and the water will turn deep brown with hydric sulphide, and yield a yellow precipitate with potassium chromate. The presence of sulphates or chlorides hinders the solution, so that hard waters may be more safely passed through lead pipes and stored in lead cisterns for domestic use. Christison asserts that all salts impede the action, and nearly in the inverse ratio of the solubility of the compounds which their acid forms with lead oxide. Some salts, when in comparatively strong solution, assist the action, which in weaker solution they impede. Sodium carbonate renders even a hard water capable of attacking lead, its bicarbonate does not. Lead cisterns should be soldered autogenously, and carefully protected from galvanic action. According to Carter Bell, pure water dissolves 0·946 of plumbic chloride, and the addition of hydrochloric acid up to 14 per cent. decreases the solubility of this salt; afterwards more acid increases it. The presence of ammonium nitrate and nitrates increases in a marked degree the solubility of lead, even in the presence of salts which would otherwise protect it from solution. Kaiser kept freshly cut strips of lead in a bottle of sea water for four days, the bottle being frequently shaken. No trace of lead could be detected in the water, but the bright surface of the strips was coated with an insoluble lead compound. He concludes that lead pipes may be used in marine aquaria without any fear of injury to their inhabitants. A valuable contribution to the action of saline solutions upon lead was made by Pattinson Muir in 1872, who shows that comparatively small quantities of pure nitrates (especially ammonium nitrate) dissolved in a large quantity of water, causes that water to exercise a very powerful solvent action upon lead. Pure distilled water dissolves about 2 milligrams. of lead per litre after twenty-four hours exposure of the lead to the action of the water. Loch Katrine water (as supplied to Glasgow) dissolves about half as much lead as this. If a very small quantity of a soluble carbonate be present the action of this solution on lead is scarcely perceptible. So, also, if to a water containing nitrates there is added a small quantity of a carbonate, the action which, were nitrates alone present, would be exercised on the lead, is rendered very much less energetic. Chlorides act like carbonates, but not to so great a degree, and sulphates also act in a similar manner. The result of the experiments are embodied in the following table:—

Name of Salt in Solution.	Grams. per Litre.	Grains per Gallon.	Lead Dissolved.					
			Grams. per Litre.			Grains per Gallon.		
			24 Hours.	48 Hours.	72 Hours.	24 Hours.	48 Hours.	72 Hours.
Ammonium nitrate,	·02	1·4	13	—	25	·91	—	1·75
" "	·04	2·8	15	15	32	1·05	1·05	2·24
" "	·08	5·6	15	—	—	1·05	—	—
Potassium nitrate,	·02	1·4	2	2	—	·14	·14	—
Sodium sulphate,	·05	3·5						
Potassium nitrate,	·04	2·8	·8	1	1·2	·05	·07	·08
Sodium sulphate,	·212	14·7						
Potassium nitrate,	·045	3·1	—	—	·3	—	—	·021
Sodium carbonate,	·308	21·5						
Potassium nitrate	·078	5·4	—	—	·5	—	—	·035
Potassium carbonate,	·504	35·2						
Calcium sulphate,	·252	17·5	·4	—	·8	·02	—	·05
" "	·458	28·5	·4	—	1·0	·02	—	·07
Potassium carbonate,	·31	21·7	—	—	·2	—	—	·014
" "	·516	36·1	—	—	·2	—	—	·014
Calcium chloride,	·25	17·5	·5	·5	·5	·04	·04	·04
" "	·51	35·7	·3	—	·4	·028	—	·028
Sodium sulphate,	·20	14·0	—	—	·8	—	—	·05
" "	·40	28·0	—	—	·5	—	—	·03
Ammonium nitrate,	·02	1·4	—	—	1·8	—	—	·126
Calcium nitrate,	·06	4·2						
Ammonium chloride,	·02	1·4						
Potassium carbonate,	·10	7·0	—	—	·4	—	—	·028
Sodium sulphate,	·20	14·0						
Sodium sulphate,	·20	14·0						
Potassium carbonate,	·04	2·8	—	—	·1	—	—	·007
Calcium chloride,	·10	7·0						
Loch Katrine,	—	—	1	1	1·5	·07	·07	·105
Distilled water,	—	—	2	2	3	·15	·15	·21

Analysis. — Miller recommends the following method for detecting lead in water:—Acidify with a few drops of acetic acid, and add one-twentieth of the volume of water of a saturated solution of hydric sulphide in a 10-inch glass cylinder; a brown coloration will be evident when a very minute quantity is present. It is as well to compare it with the water not having had the reagent added. For quantitative analysis a standard solution may be made for comparison, containing 0·1831 grams. of crystallized sugar of lead to 1 litre of water.

For the analysis of metallic lead it is requisite to employ a large quantity, as the impurities contained do not often amount to 1 per cent. For refined

lead at least 2000 grains should be employed. After weighing, it is convenient to melt the lead in a Berlin porcelain crucible, and to granulate it by pouring into a large beaker full of distilled water; the crucible with lead adhering to it is added when cold. The quantity of water should measure about 1 quart. About $1\frac{1}{2}$ pint of this water is poured off the lead, and nitric acid added to the remainder to effect solution. When quite dissolved the crucible is removed; the solution is poured into a capacious evaporating dish, and evaporated to dryness to remove the excess of acid. Upon re-dissolving in water a white residue is generally obtained, which may be collected and weighed on a tared filter. This insoluble matter may be lead sulphate, and antimony and tin oxides. The sulphate may have been produced by traces of hydric sulphate in the nitric acid used, so that if it is an important fact to determine a blank experiment should be made. The residue may be treated with ammonium sulphide, and the antimony and tin obtained in solution. On acidifying they are precipitated as sulphides, and may be weighed together. Their separation from lead oxide and sulphate may also be accomplished by TOOKEY'S method after oxidation with fuming nitric acid. This consists in passing a current of dry hydrochloric acid over the oxides, to convert them into chlorides; after which the application of a gentle heat will volatilize the chlorides of tin and antimony, which may be condensed in a beaker of water, whilst the plumbic chloride remains behind. Antimony is now precipitated by metallic iron, and the tin subsequently by hydric sulphide.

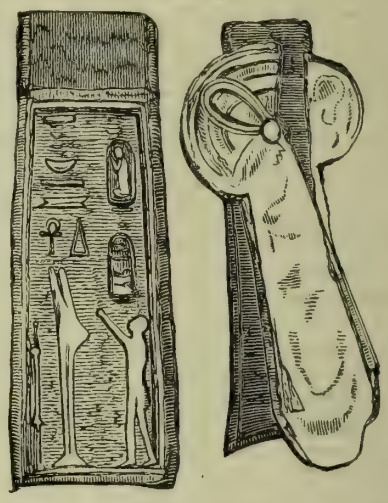
The solution of lead nitrate, containing probably copper, silver (bismuth), iron, nickel, and zinc, is warmed, and hydric sulphate added until all the lead is precipitated; a drop or two of hydrochloric acid is added to throw down the silver. Upon subsidence of the dense white precipitate, the clear fluid is decanted, washed, and evaporated with the wash water to dryness. Upon re-solution of the residue and filtration, a current of hydric sulphide is passed through to precipitate copper and bismuth sulphides. These are filtered off, and separated, after solution in nitro-hydrochloric acid, by ammonia.

After boiling off the hydric sulphide in the filtrate from the copper sulphide, the iron, after oxidation, is precipitated by ammonia, and zinc will be held in solution, from which it may be precipitated with a drop or two of ammonium sulphide. If this precipitate is dark coloured, nickel may be suspected. The silver is best estimated by cupellation. For refined lead not less than 2000 grains must be used; and if for the purpose of making white lead, it will be necessary to scorify and cupel 5000 grains, in order to get an accurate estimation of so important an impurity.

LEATHER.—French, *cuir;* German, *leder;* Italian, *cuojo;* Spanish, *cuero;* Greek, *πετζιου*; Hindoo, *chumra.* —The hide or skin of any of the warm-blooded animals, when removed from the carcase and exposed to the action of air and moisture, rapidly enters on a state of decomposition. But if the fresh skin of an animal, carefully divested of hair, fat, and other impurities, is immersed in dilute solutions of tannic acid, a chemical combination ensues; the elastic and cellular tissues gradually combine with that substance, ultimately forming an insoluble compound, incapable of putrefaction. This is leather.

The origin of the art of tanning must ever remain shrouded in the obscurity which at present veils it. The untutored savage was and is content to use the skins of animals captured in the chase in the simplest form, merely drying them in the sun, or roughly preparing them with grease or oil. Many isolated portions of the human family are at the present time ignorant of tanning. Dr. ELLIS, when in Madagascar, found to his surprise that, although the island possessed many tanning agents, yet the natives never appear to have used them for that purpose. All the islanders of the Pacific Ocean were, until a recent period, strangers to the art of tanning. This may be attributed in great measure

Fig. 1.



to the fact that, with the exception of kangaroos in Australia, all the large and small islands of Australia were destitute of mammalia with skins of size available for coverings. But the inhabitants of the great centres of civilization, such as Egypt and China, early acquired the art of preparing the skin. Tanning must have been practised by the Egyptians 2700 years since, as is evidenced by the pieces of embossed gilt leather straps taken from a mummy, and now exhibited in the British Museum. The figures on the strap represent the first or second king Orsokou adoring the god Bhem. Date, 900 B.C. (Fig. 1). In the book of Numbers, chap. xxxi. 20, after the war with the Midianites, reference is made to the purification of their raiment, and of all that pertained to skins; also in the instructions for the erection of the Tabernacle, rams' skins dyed red, and badgers' skins, are mentioned as the two outermost coverings of the sacred structure. The bottle of water which Abraham placed on Hagar's shoulder (Gen. xiv. 21), as she left his camp with Ishmael,

was probably the skin of a kid or goat, similar to those in general use among the nomadic tribes of Asia. In Herodotus mention is made that, among the motley crowd that followed Xerxes, were Ethiopians, who carried shields covered with skin, and the Thracians had their legs protected by buskins manufactured from the skins of fawns. In any attempt to ascertain the probable age of the leather manufacture the student is met by this difficulty—in the three dead languages, Latin, Greek, and Hebrew, and probably others, the words *hide*, *skin*, and *leather* are used indiscriminately. Thus in Latin *corium* stands for skin and leather; in the Greek πετζιον is vaguely employed for either. Thus in the case of the shields of ancient heroes, they were probably nothing more than a rude wooden frame, over which was stretched the thickest part of the bull's hide, namely, the shoulder; this dried in the sun, and of three layers, would be amply sufficient to ward off any ordinary sword cut. But they could not properly be designated leather shields. The skin bottles, to which reference has been made, were evidently only greased externally; they seem to have undergone no other preparation, and therefore this elucidates the meaning of David's complaint in Psalm cxix. 83: "I am like a bottle in the smoke," which would naturally deteriorate under such circumstances. Our Lord also refers to the old bottles which, having lost their elasticity, were unequal to resist the fermentation of the *new* wine. But on the other hand, the rams' skins and badgers' skins of the Tabernacle must have passed through some more elaborate process than greasing, especially if the wool and fur were retained; they may therefore be recognized as *leather*. The Jews appear to have had the same prejudice against all connection with the leather trade as most of the Eastern nations. The Talmud says, "Woe unto him whose trade is a tanner;" yet Peter, in pursuit of his missionary work, was able to rise above the common prejudice, in locating himself at the house of Simon the tanner, to which Dean Stanley, in his "Sinai and Palestine," refers as one of the few spots it is possible to identify with some degree of certainty. The waves of the sea dash against the outer wall, whilst within the court-yard rises a beautiful spring of water, furnishing that which was so necessary for his trade. The Chinese from the remotest age were acquainted with tanning. The Romans attained to considerable perfection in the preparation and finishing of leather. Boots and shoes of a finish comparable with those of the present day adorned the feet of the Roman ladies. Pliny speaks of hides tanned with bark ("cortice coria conficere"). He also mentions gall nuts, sumach, and lotus bark as employed in tanning. After the irruption of the barbarians, leather came into more general use, but the character of the manufacture was inferior. But little advance was made in the art during the dark ages. Embossed leather of considerable artistic beauty came into vogue about A.D. 1300. Specimens of it may be seen at the present day in some of our old houses, in the form of tapestry, at Blenheim, Norwich Palace, and a few other spots; these were highly coloured and gilded. Spain, Italy, Flanders, and England were each in turn celebrated for the production of these works of art. It is a matter of regret that the art has fallen into disuse. Leake, of London, has within a few years sought to revive it, having produced some very beautiful representations of fruits, flowers, &c., on embossed leather.

The statute book of England is in itself an interesting study, to notice how many well meaning but foolish enactments were passed bearing on the leather manufacture, which, far from being a blessing, hampered the tanner, and prevented any improvement in the article, so that for 300 years it may be broadly asserted the trade remained at a stand still. At the commencement of the present century the exciseman was in constant attendance at the tan-yard; not a hide was permitted to be moved without his supervision, and heavy fines were inflicted for all infractions of the law. The amount received by government for this vexatious impost was only £330,496 for 1828. In 1830 Goulburn abolished the tax on leather, which had reached £411,000. An instructive lesson may be learned from comparing the value of leather and saddlery exported in the years 1828 and 1875.

	1828.		1875
Leather,	£94,155	....	£1,442,215
Saddlery,	89,206	....	2,364,258
	£183,361	....	£3,806,473

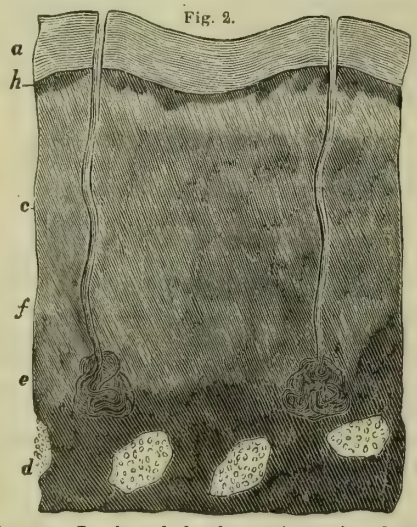
The tanners of fifty years since were men of but limited capital, scattered over the country, working under great disadvantages. They had an instinctive dread of all improvements and innovations, and were, with few exceptions, totally ignorant of the chemistry of their trade. Now large tan-yards of improved construction are gradually concentrating near the great ports where the raw materials are imported, the amount of capital invested having been estimated at £30,000,000. The chemistry of the trade has also become the subject of inquiry and scientific research, the advent of many new tanning materials demanding from the manufacturer a more extended and enlightened knowledge of the different forms of tannic acid brought before him, and of the laws which govern their right application. Science has as yet been able to effect only small results in this manufacture, as compared with its success in many others. There have not been wanting scientific men whose sympathies have been enlisted on behalf of the tanner; but the majority have too often applied their knowledge to carry out some pet theory of their own, rather than patiently work out the problems which were waiting to be solved. The time occupied in the process has been materially shortened, but the quality of the leather has correspondingly deteriorated. Rapidity with excellence of quality has yet to be attained. Within a few years considerable attention has been directed to the subject, so that many men of eminence both in England and on the Continent are engaged with it. Chemistry is quietly but surely extracting from nature the answers to

certain questions, thus laying the foundation for a more thorough knowledge of the subject. The tanner is indebted to the labours of many English and German chemists, as Davy, Calvert, Brande, Reimer, Eitner, and Schiff. Nor must it be forgotten that the different exhibitions, both in England and elsewhere, have tended to raise the standard and enlarge the ideas of the various competitors.

The Skin.—Somewhat analogous to the bark of a tree, being renewed from within as rapidly as the exterior surface is lost by wear and desquamation, the skin is divided into two distinct parts—the cuticle or epidermis, and the corium or true skin.

According to Ashe (who has written a very scientific paper on the human skin, to which we are indebted)—"The cutis, or true skin, *c*, Fig. 2, rests upon a very fine interlaced or netted structure, called the *areolar tissue*, out of which, if we may so express it, the granules and fibres of the skin are formed. The cuticle, or scarf skin, *a*, is never of any great thickness in any animal, but the true skin is of very variable

Fig. 2.



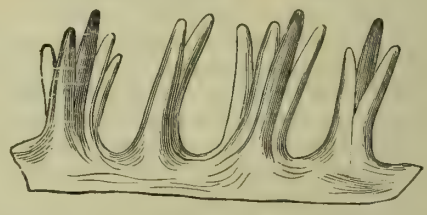
thickness. In the whale the cutis attains the thickness of about an inch, which is the greatest known in any animal. The *cuticle*, Fig. 3, consists of several layers of laminated scales, the laminated form being best marked at the very surface, where the scales are constantly falling off as a kind of scurf, and are as constantly being renewed from below. These scales are formed by the flattening out of granules more or less rounded, which is the form assumed by the particles of the cuticle in its deeper layers. These granules are at first nucleated cells, and the colouring matter of the skin resides in the nuclei; and these granules it was that were formerly described as a separate layer under the name of *rete mucosum*, *h*, Fig. 2. They are very minute, being about $\frac{1}{3000}$th of an inch in diameter at first. Being removed from below as the flattened scales are removed above, they gradually approach the surface, and as they do so they more and more lose the granular form, and assume the scaly character, their diameter increasing accordingly to about $\frac{1}{600}$th of an inch. Into the epidermis, or cuticle, no nerves or blood-vessels penetrate, and it is nourished merely by the transudation of the serum of the blood through the walls of the vessels of the true skin and subcutaneous areolar tissue. It is not itself sensitive, but, on the contrary, serves to blunt the too exquisite sensation of the true skin. Next we come to the structure of the cutis, or true skin, *c*, Fig. 2, which is much more highly organized, and consists of two kinds of tissue—namely, white and yellow fibres; the former being denser and more resisting, and being therefore present in greater quantity wherever resistance is most needed, as in

Fig. 3.



the palm of the hand and sole of the foot; while the yellow fibres are a highly-elastic tissue, owing to their minute fibrillæ being arranged in interlacing curves; and these fibres cross each other repeatedly, and branch, so as to form lozenge-shaped interstices, which are filled up principally by the white fibres. These yellow fibres accordingly, as might be anticipated, exist in greater abundance where elasticity is a special requirement, as at the flexures of the joints, the lips, &c. The uppermost surface of the cutis, or true skin, is strangely uneven

Fig. 4.



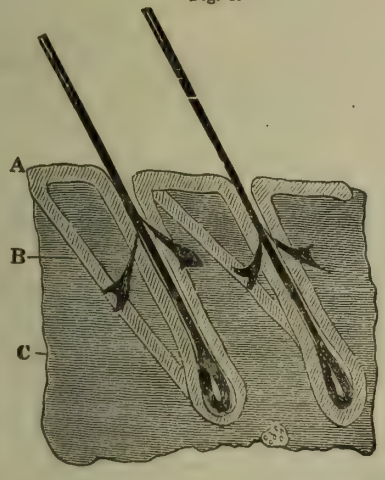
and irregular" (this surface is technically known as the *grain* of a skin, Fig. 4, and will often be referred to hereafter as the cause of much anxiety to the tanner), "being elevated into a vast number of minute papillæ, which are about $\frac{1}{100}$th of an inch in height, and $\frac{1}{250}$th of an inch in diameter. Minute as these little papillæ are, each possesses a ramification of vascular capillaries and of nerve fibres, being, in fact, the essential agents in the sense of touch, for that is the function of these papillæ. The skin of the tongue in men and animals show the papillæ much larger than in any other part of the body. The true skin is perforated by perspiratory ducts, *f*, Fig. 2, and

when the hand is warm the perspiration may be observed even with the naked eye to issue from them, forming minute shining dots. The glands, *e*, Fig. 2, by which the perspiration is secreted are seated at the under surface of the true skin, each embedded in a cavity of it. These glands are consequently to be regarded as true excretory organs, removing from the blood materials that are no longer wanted, and which if retained would be injurious. About 2500 of these ducts are found in 1 square inch of the skin."

"Another kind of gland is also found in the skin in connection with the hairs, and engaged in their nutrition; these glands are called sebaceous glands, *d*, Fig. 5; the ducts of these glands are not spiral, and they open generally into the hair follicles or pits in which the hair grows out of, situated in the subcutaneous areolar tissue; these glands lubricate the skin, and so maintain its elasticity; and they also eliminate hydrocarbons from the system."

The first aim of the tanner is to swell the true skin, to remove the cuticle with the hair, and thus

Fig. 5.



prepare the pelt for the tanning process. The skin, on maceration in water for any length of time, undergoes the following changes: the mucous layer is dissolved, rendering the epidermis loose, which speedily separates from the corium, carrying the hair with it. This action is rendered more rapid on the addition of alkalies to the water. The extractive matter of the true skin is also soluble in the water, leaving the fibres as a network, in which condition, if carefully dried, it becomes semi-transparent, not unlike parchment. It is a matter of doubt how far the albuminous portion of the corium should be wholly dissolved, and whether a portion of it may not be retained with considerable benefit to the future leather. Also, whether skin which is subjected to the action of alkalies, such as lime, does not deteriorate from the fact that all the extractive matter has been destroyed, leaving the structure of the skin spongy and porous. Reimer has lately published the results of his experiments on skin, which may be briefly summarized as follows:—His first object was to ascertain the nature of the substance which glues together the fibrous web of the raw hide. After carefully preparing a piece of skin by repeated washings, until the last water gave no precipitate with ferrocyanide of potassium, the skin was steeped in lime water for a week in a stoppered bottle; this lime water, after the removal of the skin, was treated with hydrochloric acid, when a flocky precipitate separated, which when dried had much the appearance of albumen. He also found that skin steeped in 10 per cent. of salt solution yielded the same precipitate on the addition of acids. This new substance, which he named *coriin*, is insoluble in water, soluble in alkaline solutions and in strong hydrochloric acid. Chloride of iron does not precipitate coriin; but it is readily precipitated by persulphate of iron. Oak-bark tannin precipitates all the coriin in acid solutions; but in alkaline sufficient tannin must be employed to render them neutral. Gallo-tannin acts in a similar manner. The fibrinous portion of the skin he next examined, which was treated with one-half per cent. solution of acetic acid; the skin was considerably swollen, and rendered semi-transparent. After a few days the acid solution was treated with salt, when a fibrous precipitate, something like coriin, was separated. But this precipitate was insoluble in lime water, soluble in boiling water, and formed a strong jelly. It was also soluble in excess of strong alkalies, being precipitated from acid solutions by tannin and persulphate of iron. This leads us to one conclusion, that the skin when prepared by the ordinary process for the tanner has the coriin in such a condition, that unless great care be taken in the manipulation of the skin much waste of the albuminous substance of the pelt is inevitable. Both the fibrin of the skin, with the coriin, and also albumen, are especially precipitated by tannin, or in other words form a chemical compound, a *tanno-gelatin*, which is imputrescible, and at the same time elastic. This chemical combination we name *leather*. Other substances, such as alum and sulphate of iron, also combine with the gelatin of the skin; but the combination is one of a weaker character. All these compounds pass under the name of leather; but that of *tanno-gelatin* is especially recognized as such, and employed in the various manufactures of boots, shoes, belting, and saddlery. Having thus passed under review the skin, it will be necessary to glance at the different tanning materials.

Tanning Materials.—The art of tanning was practised long before its first principles were discerned; like most of our great manufactures, it is very probable, if it were possible to trace it to its origin, it would be found to be the outcome of some accidental discovery. Pliny speaks of Tychius of Bœotia, who is said to have made Hector's shield with the hides of seven oxen. He also mentions gall nuts, alum, lotus bark, and sumach as being used in his time for tanning.

It remained for chemists of later times to open up the science of tanning, and in their researches lay bare the first principles of the art. Seguin was the first to publish the results of his experiments. This chemist showed that the acid solution which he

obtained from digestion of gall-nuts in boiling water was distinct from gallic acid, as it had the property of combining with animal matters, such as albumen, gelatin, and starch, forming with them insoluble compounds. Davy, Brande, and Stenhouse in England have added to our knowledge in this matter; Liebig, Berzelius, Erdmann, Reimer, and Schiff, on the Continent, have each given their quota.

Tannic acids are very widely diffused over the vegetable kingdom; from all parts of the world is it brought to our shores. It is asserted by Morfit that tannin only exists in perennial plants, and is not found in poisonous plants, or such as give a milky sap. It is found in the bark of some trees, in the leaves and fruits of others, and in some cases the dried sap is made available for tanning purposes. Subjoined is a list of most of the plants employed in tanning in different parts of the world, compiled from list furnished by the late W. G. Fry and Professor Bernardin:—

Vernacular Name.	Scientific Name.	Part of Tree Used.	Remarks.
BRITISH ISLES.			
Oak,	Quercus pedunculata,	Bark.	
"	" robur,	"	
Larch,	Larix europæa,	"	
Alder,	Alnus glutinosa,	"	
Tormentil,	Tormentilla potentilla,	Root.	
FRANCE.			
Kermes,	Quercus coccifera,	Bark.	
Dentelarie,	Plumbago europæa,	Bark of root.	
Willow,	Salix alba,	Bark.	
"	" cinerea,	"	
Sumach,		Leaves.	
SPAIN.			
Cork tree,	Quercus suber,	Bark,	Inner bark.
Chesnut,	Castanea vesca,	Bark and extract.	
Alder,	Alnus glutinosa,	Bark.	
Aleppo pine,	Pinus excelepensis,	"	
Stone pine,	" pinea,	"	
ITALY.			
Cork tree,	Quercus suber,	Bark,	Sardinia.
Holm tree, or green oak,	" ilex,	"	Tuscany.
Sumach,	Rhus coriaria,	Leaves,	Sicily.
Olive,	Olea europæa,	Bark.	
Myrtle,	Rhus myrtifolia,	"	
Knoppern,	Quercus pubescens,	Galls	Also Hungary.
TURKEY.			
Valonia,	Quercus ægilops,	Acorn,	Smyrna.
Galls,	" infectoria,		
RUSSIA.			
Birch,	Betula alba,	Bark.	
Marsh rosemary,	Statice coriaria,	Root.	
Bearberry,	Arctostaphilos uva ursi,	Leaves.	
BRITISH GUIANA AND WEST INDIES.			
Mora,	Mora excelsa,	Bark.	
Seaside grape,	Coccoloba uvifera,	"	
Kararalli,	Lecythis ollaria,	"	
Cuyama,		"	
Kullaballi,		"	
Arrasa,		"	
——,	Bucida buceras,	"	
Hog plum,	Spondias lutea,	"	
Sirnabelli,	Nectandra,	"	
Baramalli, or pump wood,		"	
Courida,	Avicennia nitida,	"	
Divi divi,	Cæsalpinia coriaria,	Seed pod.	
Blood wood,		Bark.	
Crab wood,	Carap guianesis,	"	
NORTH AMERICA.			
Chesnut,	Castanea,	Bark.	
Quercitron,	Quercus tinctoria,	"	
Statice, marsh rosemary,	Statice coriaria,	Root.	
Larch,	Larix americana,	Bark.	
Hemlock,	Abies canadensis,	Bark and extract.	
——,	Geranium maculatum,	Root.	
Water plantain,	Polygonum amphibium,	"	
NEW ZEALAND.			
Towhai,	Weinmannia racemosa,	Bark.	
Hinan,	Elœcarpus dentatus,	Bark and extract.	

Vernacular Name.	Scientific Name.	Part of Tree Used.	Remarks.
NEW ZEALAND—(*Continued*).			
Tarsekeha,	Phyllocladus trichomanoides,	Bark.	
Red birch,	Fagus menziesii,	"	
———,	Coriaria ruscifolia,	"	
———,	Eugenia maire,	"	
AFRICA.			
Saffron,	Crocoxylon excelsum,	Bark.	
Doomboom,	Acacia horrida,	"	Cape.
Wagenboom,	Protea glandiflora,	"	"
Krupelboom,	Leucospermum conecarpum,	"	"
Almardelboom,	Beabejum stellatum,	"	"
Purimbas,	Fusarmis compressus	"	"
———,	Acacia vera,	"	Egypt.
Neb neb,	" nilotica,	Seed pod,	Nubia.
———,	" sabac,	"	"
———,	Solanum marginatum,	Bark,	"
Kino,	Pterocarpus marsupium,	Extract.	
Boomah,	Pyenocama macrophylla,	Nut,	Port Natal.
Squills,	Scilla maritima,	Bulb,	Algiers.
EAST INDIES.			
Tamarisk galls,	Tamarix indica,	Galls,	Native name of T. indica, Sumrut-ul-toorfa,
Saul tree,	Shorea robusta,	Bark.	
Betel,	Areca catechu,	Nut.	
Gambier,	Uncaria gambir,	Extract.	
Kassu,		"	
Cutch,	Acacia catechu,	"	
Butea kino,	Butea frondosa,	"	
Asacum,		"	
Palachy,	Butea superba,	"	
Mochrus,	Bombax malebarica,	"	
Adurla,	Phylanthus emblica,	Seed pod.	
Terce,	Cæsalpinia,	"	
Myrabolans,	Terminalia cherbula,	Fruit.	
"	" angustifolia,	"	
"	" belerica,	"	
Gaub,	Diospyros glutinosa,	"	
Sogah,		Bark.	
Samak,		"	
Babool,	Acacia arabica,	"	
Turwar,	Cassia amiculata,	"	
Pomegranate,	Punica granatum,	"	
Subaujuna,	Moringa pterygosperma,	"	
———,	Careya arborea,	"	
Tangede,		"	
Huldi,		"	
SOUTH AMERICA.			
Divi divi,	Cæsalpinia coraria,	Seed pod,	Rio Lache.
Algarobiall,	Prosopis pallida,	"	Valparaiso.
Cascara,		Bark,	Panama.
Tuinbo colorado,		"	"
Curmpuay,		"	Corrientes.
Cevil,		"	Cordova.
Molle,		Leaves,	"
Tuga veca,		Extract,	Brazil.
———,	Stryphuodendron barbtaiman,	"	"
———,	Mesembyranthemum nodiflorum,	Bark,	"
Murici,	Brysonima,	"	"
White mangrove,	Avicennicia tomentosa,	"	"
Rhatany,	Krameria triandria,	Root,	"
———,	Luhea grandiflora,	Bark,	"
Quebracho,	Aspidospermum quebracho,	"	River Plate.
Balsamo,	Carpon brevifolium,	Seed pod,	Chili.
AUSTRALIA AND TASMANIA.			
Silver wattle,	Acacia dealbata,	Bark.	
Black wattle,	" mollissima,	"	
Black wood,	" melanoxylon,	"	
Honeysuckle,	Banksia australis,	"	
Tasmanian laurel,	Anopterus glandulosa,	"	
Sassafras,	Atherosperma moschata,	"	
Cherry tree,	Exocarpus cupressiformus,	"	
She oak,	Casuarina quadrivalis,	"	
Celery-topped pine	Phylocadus asplenifolia,	"	
Myrtle,	Fagus cunninghami,	"	
Aru Mata,		"	
Arok kenema,		"	
Blue gum,	Eucalyptus globulus,	"	
Iron bark,	" resinifera,	Extract.	

The active astringent principle which characterizes these plants have one property in common, that they unite with gelatin and albumen, forming insoluble compounds. Chemists have discovered that the tannin of certain plants, such as oak-bark, valonia, and nut-galls, when treated with solutions of persalts of iron, give bluish-black precipitates. To this kind of tannin they give the name gallo-tannic acid. A second variety, including sumach, catechu, and the tea plant, give under similar circumstances an infusion of a greenish-black tint. The colour of the precipitate is, however, much influenced by other external circumstances, so that it cannot be relied on for giving any clear definition, nor has it led to any practical results. Dr. Stenhouse has contributed to the subject much valuable information. He endeavours to prove that all tanning substances may be defined as belonging to one of two classes. The first is that of those tanning principles in which the tannic acid is prone under favourable circumstances to degenerate into gallic acid, and also yield pyrogallic acid when submitted to destructive distillation. Among these are reckoned sumach, divi-divi, valonia, and myrabolans. The other class of tannins do not contain gallic acid, nor when subjected to destructive distillation is pyrogallic acid the product. Among these are prominent gambier and mimosa bark. The proneness of the first class of tannic acids to turn into gallic acid under ordinary conditions, and the loss occasioned thereby to the tanner, makes this question one of vital importance to the trade. It will therefore be necessary to pass under review both gallic and tannic acids.

Gallic Acid, Dioxysalicylic acid, $C_6\begin{cases}H_2\\(OH)_3\\CO.OH\end{cases} = C_6H_7O_5$.—This acid, which was discovered by Scheele, exists ready formed in many plants, and is obtained by the metamorphosis of gallo-tannic acid. It is contained in sumach, in hellebore root, in divi-divi, in the acorns of *Quercus ægilops*, in green and black tea, in *Uva ursi* leaves, in sandal-wood, and in colchicum.

To obtain it from plants which at the same time contain tannin, an infusion of the plant is precipitated with gelatin; the liquor separated from the filtrate is evaporated to dryness and exhausted with alcohol; the alcoholic solution is evaporated, and the residue is exhausted by boiling water, which on cooling deposits gallic acid in crystals. They are purified by recrystallization and treatment with animal charcoal. Gallic acid is, however, much more conveniently obtained by the metamorphosis of gallo-tannic acid. The powdered galls are mixed with water, exposing the mixture to the action of the air for some weeks at a temperature of 70° to 75° Fahr., now and then adding water till the mass swells and becomes mouldy. When subjected to pressure a coloured liquid is the result; the residue boiled with water and filtered while hot, on cooling deposits needle-like crystals of gallic acid, which may be purified by redissolving and boiling with a little animal charcoal. Gallic acid requires for solution 100 parts of cold water and only 3 parts of boiling water; the solution has an acid and astringent taste, and gradually decomposes by keeping. Gallic acid does not combine with gelatin. Brande mentions that the effect of heat on gallic acid is very peculiar. If heated in a retort to a temperature of 410° to 420° Fahr. carbonic acid is evolved, and the upper part of the retort soon becomes studded with white crystalline particles, constituting a new acid, termed by M. Deyeux, its discoverer, the *pyrogallic* (pyrogallol, $C_6H_6O_3$). If the heat be suddenly raised to 480° Fahr. the results are different; carbonic acid is still disengaged, but instead of a sublimation of crystalline matter, water is evolved, and the retort is ultimately found to contain a considerable amount of brilliant dark-coloured material, termed *metagallic acid* ($C_6H_4O_2$). If a dilute infusion of gall-nuts be exposed to atmospheric contact for a long time, not only is gallic acid precipitated, but *ellagic* also. This *ellagic acid* ($C_{14}H_6O_8$) is one of the results of the tanning process. The tawny powder, almost insoluble in water, alcohol, and ether, is technically known as *Bloom*.

Gallo-tannic Acid ($C_{27}H_{22}O_{17}$).—Stenhouse has shown that most of the tannins which give bluish-black precipitates with ferric salts are glucosides, that is to say, they are resolved by boiling with dilute acids into glucose and gallic acid; few give no gallic acid. Whereas, among those which give green precipitates with ferric salts, only one, namely, the tannin of willow bark, appears to be a glucoside. Gallo-tannic acid is especially distinguished by yielding pyrogallic acid when heated.

Preparation of Gallo-tannic Acid.—A percolating apparatus is half filled with finely-pulverized gall-nuts, and commercial ether, containing water and alcohol, is poured in. The liquid separates into two layers, the lower of which is a heavy, syrupy, amber-coloured solution of tannic acid, water, and ether, while the upper is mobile, consisting of ether, water, gallic acid, and a small quantity of tannic acid. Ether is poured into the apparatus as long as the lower stratum continues to increase; the upper layer is then removed, and the lower is repeatedly washed with ether, and dried *in vacuo*. Gall-nuts thus treated yield from 35 to 40 per cent. of tannic acid (Pelouze).

Properties.—Gallo-tannic acid is a colourless amorphous mass, remaining, when its aqueous solution is evaporated, in transparent, vitreous, shining, fissured, easily friable lumps. It is inodorous; has a strongly astringent taste, not at all bitter; reddens litmus; does not soften between the fingers. It acquires a yellow colour by exposure to light, even in closed vessels. It does not act on polarized light. Gallo-tannic acid dissolves readily in water, forming a colourless frothing liquor. The following table shows the specific gravity of aqueous gallo-tannic acid at 15° C., according to Hammer (*J. pr. Chem.* lxxxi. 159):—

Per Cent.	Spec. Gravity.	Per Cent.	Spec. Gravity.
1	1·0040	6	1·0242
2	1·0080	7	1·0283
3	1·0120	8	1·0325
4	1·0160	9	1·0367
5	1·0210	10	1·0409

Gallo-tannic acid is precipitated unaltered from its aqueous solutions by several *salts*, as *sal ammoniac*, *common salt*, *sulphate*, and *acetate of potassium* (not by nitre or glauber salts, according to Strecker); by *sulphuric* and *hydrochloric* acids (Berzelius); from very concentrated solution by *phosphoric*, *oxalic*, and *tartaric* acids (Wackenroder); and by *arsenic* acid (Berzelius). When *boric* acid is dissolved with aid of heat in aqueous tannic acid, the mass solidifies on cooling to a white jelly, which dries up to a bulky snow-white mass (Berzelius). These precipitates were regarded by Berzelius as compounds of tannic acid with mineral acids; but the precipitate thrown down by sulphuric acid retains, after pressure, only a small and variable quantity of sulphuric acid; that produced by hydrochloric acid gives off all its hydrochloric acid *in vacuo* over quicklime: hence the precipitates can be regarded only as mixtures of tannic acid with mineral acids, produced because tannic acid is less soluble in acidulated than in pure water (Strecker).

Decompositions.—Gallo-tannic acid heated to 150° or 160° C. becomes darker from incipient decomposition; at 215° it is resolved into water, carbonic anhydride, and pyrogallic acid, which volatilize, and metagallic acid, which remains; at 250° only metagallic acid is formed, without pyrogallic acid (Pelouze).

Gallo-tannic acid, heated in a platinum spoon, decrepitates, undergoes semifusion, swells up, carbonizes, takes fire, and burns with a bright flame (Berzelius). Exposed on a watch-glass to strongly *ozonized air*, it acquires a yellow or yellow-brown colour, becomes glutinous and fluid, strongly acid, from formation of oxalic acid, and if the action be continued long enough, disappears completely, being converted into water and carbonic acid (Schönbein). When a very dilute aqueous solution of gallo-tannic acid is exposed to the *air* it becomes turbid from the separation of grey crystalline gallic acid; oxygen is absorbed at the same time, and an equal volume of carbonic anhydride is produced (Pelouze).

Aqueous gallo-tannic acid, evaporated with aid of heat in open vessels, leaves a brown translucent mass, which when treated with water leaves a dark-brown residue. This residue is the *oxidized tannic acid* of the older chemists. By *permanganate of potassium* aqueous gallo-tannic acid is rapidly oxidised, the solution, if concentrated, giving off carbonic anhydride. One milligramme of gallo-tannic acid dissolved in a litre of water is sufficient to decolorize the acid solution of the permanganate (Monier). Aqueous gallo-tannic acid, which remains unaltered when not exposed to the air, decomposes with evolution of carbonic anhydride and formation of gallic acid, if it remains in contact with the nitrogenous constituents of the gall-nuts; therefore in infusion of gall-nuts, and more quickly in gall-nuts moistened with water (Pelouze). Ellagic acid is formed at the same time; the formation of mould, which commonly takes place, has no influence on the transformation. The decomposition takes place even in closed vessels, and more quickly as the solution of tannic acid is more dilute (Robiquet). The transformation may be regarded as a fermentation process, inasmuch as it is stopped or retarded by antiseptics, as alcohol, wood vinegar, creosote, and corrosive sublimate. The pectase of the gall-nuts is the ferment which excites the gallous fermentation, and the simultaneous conversion of the pectose into pectin. Emulsin, yeast, vegetable or animal albumen, and legumin, retard rather than promote the gallous fermentation (Robiquet).

Through the researches of Dr. Schiff a new light dawns on the formation of these two acids. The science of organic chemistry is entering on a new phase, and every day furnishes fresh evidence of the truth that we are on the threshold of great discoveries. The supposition prevailed some years since, that it was impossible to build up the compounds of organic chemistry from their original elements, as is done continually with inorganic, because of some supposed vital force which the chemist could not create—now, however, that theory is proved to be fallacious, as organic bodies of complete structure are daily produced in the laboratory, the expense alone being the only barrier to great revolutions in our social and commercial relations. Dr. Schiff has plainly demonstrated that gallic acid is a derivative of the phenyl series of alcohols: thus, phenol, $C_6\begin{cases}H_5\\OH\end{cases}$, or phenylic alcohol, gallic acid, $C_6\begin{cases}H_2\\(OH)_3\\CO.OH\end{cases}$ The theory that previously prevailed, that gallic acid was the result of the loss of oxygen by tannic acid, is proved to be incorrect. Dr. Schiff is of opinion that tannic acid is an etheric anhydride of gallic acid, or digallic acid,

$$C_6\begin{cases}CO,OH\\H_2\\OH\\OH\end{cases}\left.\begin{matrix}O\\CO\end{matrix}\right\}C_6\begin{cases}H_2\\OH\\OH\\OH\end{cases}$$

in other words, two atoms of gallic acid, minus one atom of water, constitute one atom of tannic acid. He has succeeded so far as to be able to produce tannic acid from gallic, by the following process:—Gallic acid is mixed with oxychloride of phosphorus, and heated at first to 100° C., and afterwards to 120° C.; hydrochloric acid is disengaged, and simultaneously a yellow pulverulent matter formed. If this be washed in dry ether and dissolved in water, in a few hours crystals of gallic acid will separate. These are collected on a filter, and to the coloured filtrate is added chloride of sodium, which has the effect of throwing down a resinous matter which can be easily collected. This resinous extract is dried *in vacuo* and dissolved in the least possible quantity of alcohol, to which ether is afterwards added and evaporated, and the result dried in vacuo. The product thus obtained has all the properties of

tannic acid, and does not contain a trace of glucose. When treated with water and hydrochloric acid it is entirely converted into gallic acid (*J. applied Chemistry*). SCHIFF observes that this is the first tannin which has been obtained free from glucose or grape sugar, of which more or less is always contained in the natural tannin. He further states that this applies to the tannin of gall-nuts and sumach. Those of oak bark, valonia, catechu, and mimosa, are but imperfectly understood, and are evidently differently constituted, as none of them can be changed into gallic acid. It will be apparent that the discovery of Dr. SCHIFF opens the door to great changes in our estimation and treatment of tanning materials. If the experiments of the laboratory can be cheaply and efficiently carried out in the tanyard, the result will be a great saving to the trade, as the loss from the decomposition of tannic acid must be enormous.

A rough summary has been previously given of the different tanning agents, such as are known to be grown or employed for tanning purposes in many countries. The enhanced price of most tanning agents, consequent on the great development of the leather trade, has stimulated the inquiry for other agents to supply the demand. Some enumerated on the list are of great strength in tanning properties; but at present the production is often limited, so that they cannot be reckoned as marketable commodities. A brief review of the different kinds will be appropriate here.

BARKS.—The bark of trees has been associated with tanning from the earliest period; and notwithstanding tanning agents of greater strength are in constant use, yet the bark of the oak stands without a rival in its capacity to produce leather of the best quality. The bark of the majority of European trees contains tannic acid; but the percentage of many is so small, that the number which are available are limited to five or six. The bark of the elm, birch, poplar, willow, and beech, have been employed by tanners in the olden time. But their use now is confined to a little larch and willow bark in Scotland.

Oak Bark.—The epidermis of the *Quercus robur*, *Quercus pedunculata*, and *Quercus sessiliflora*, in all its different stages of growth, from the bushy undergrowth of the copse to the lordly tree of the park, is available for tanning. The quality of the bark varies considerably, the trees growing on good clayey soil yielding bark of a better kind than those which grow on calcareous soils. The aspect, also, has much to do with the quality; the bark removed from trees having a southern aspect is much to be preferred. MÜLLER'S analyses of oak bark show that the oak at fifty years' growth gives 13 per cent. of tannin; at one hundred years' growth it gives 8 per cent. of tannin. As the sap rises, after its long winter slumber, giving evidence of its presence by the thickening of the buds, many a hill-side of Great Britain is invaded by a small army of hardy pioneers. The quick strokes of the axe awakening the echoes from crag to crag, the aromatic fragrance of the partially dried bark, with the busy scene of the boys and women engaged in removing the bark from the fallen trees, are reminiscences of early spring refreshing to look back on, but rapidly becoming a thing of the past. The different ages of the trees give barks which are known in the trade as coppice, flittern, store, and timber barks. The coppice bark, obtained from the bushy undergrowth of plantations about twelve years' growth, gives the purest, the exterior being very clean, and the epidermis thin; but as the tree advances in age, we come to the store bark, taken from trees of 6 to 9 inches in diameter; fifty years' growth, when the bark may be said to be in its best condition, yielding the largest amount of tannic acid: in some favoured samples 18 per cent of tannic acid is given. As the tree progresses the epidermis rapidly thickens, and the quality of the bark deteriorates. It is estimated that 200,000 tons are consumed yearly in Great Britain, besides 30,000 tons which are imported from the Continent.

According to STENHOUSE, oak bark does not yield pyrogallic acid when subjected to destructive distillation, from which we may conclude that the tannin of oak bark is not identical with that of galls. During the process of tanning, the infusion of oak bark, after exposure to the air, deposits a drab-coloured powder (*ellagic acid*), known in the trade as *bloom*, which deposit is considered essential to all good leather.

Cork Tree (*Quercus suber*).—The inner layer of bark which remains after the removal of the cork, which is the rough and dead epidermis, is of a redder colour than oak bark, with a granular texture; it contains about 10 to 12 per cent. of tannin. The quantity imported varies considerably, from 8000 to 10,000 tons being the average. It is principally used in Ireland.

Mimosa, Wattle Bark (*Acacia dealbata*), with two or three other varieties, is indigenous to Australia. The bark is of a closer texture than that of oak, the inner surface of a bright red, the epidermis varying in colour from light to dark brown. Fifty years since it was introduced to the notice of English tanners in the form of an extract, which was unsaleable. Since then the bark has been imported in large and increasing quantities. It comes in the long rind, chopped and ground. The quantity we receive is about 10,000 tons yearly. A good sample will give 24 per cent. of tannic acid. Coming to our shores in the roughly ground condition, it affords the opportunity for admixture of other inferior barks and rubbish, which was resorted to by many shippers at the outset. Unless very finely pulverized, it requires hot water to extract all its tanning properties. Mimosa does not change to gallic acid; or rather, the tannic acid of mimosa does not undergo the same decomposition as other tanning agents. The clear red liquor has considerable penetrating power, but the colour prevents any large quantity being employed. The leather made with it is hard, and rather disposed to be brittle in wear.

Oran, or African Bark, is a bark of brownish-red colour, which has recently been imported, arising from

the high price of other tanning materials. It gives a percentage of 15 of tannin. The import for 1875 was 1327 tons.

Mangrove Bark (*Rhizophora mangle*).—This tree abounds on the rivers and estuaries of India, where it grows to the height of 50 feet, spreading out its roots in all directions in the moist soil. The mangrove appears to thrive in brackish water. As the muddy deposits at the mouth of the tropical rivers become consolidated, the mangrove takes possession even to the verge of the salt water. All parts of the tree appear to be useful for tanning; the bark, roots, and leaves have been so applied. An attempt was made some twenty years since to introduce the bark to this country, but the dark brown colour which it imparted to the leather prevented its permanent use. It contains about 17 per cent. of tannic acid. Of its chemistry we are entirely ignorant.

Roots. — *Tormentilla* (*Tormentilla potentilla*) — growing in the Faroe and Hebrides Islands—was formerly employed for tanning. Loudon states that in the isles of Tiree and Coll so much land was destroyed in digging for the roots, that the inhabitants were prohibited the use of them. Müller gives the percentage of tannin as 31·25. The leather manufactured with it is reputed to have been very superior.

Marsh Rosemary (*Statice coriaria*), growing abundantly in the south of Russia, has been for centuries employed by the Kalmucks for tanning. It is also similarly employed in the Spanish tanneries. The root is deeply embedded in the earth; sometimes it is 3 yards in length, with a thickness of from 1 to 5 inches. According to Hammer's process, the root yields 20·25 per cent. of tannin; with Lowenthal's method of analysis, 24 per cent. In Russia it appears never to be used alone, but always in conjunction with willow bark.

Ratany Root (*Krameria triandria*) is a native of South America, growing in mountainous districts of Brazil and Peru, flowering at all seasons. As found in commerce, it is met with in small pieces of irregular size. The bark is of a dark yellow or brown colour, readily separates from the wood, the woody part being of a redder colour. Morfit states that the bark steeped in boiling water gives an infusion of a deep brown colour, which is abundantly precipitated by mineral acids; the alkalies only change its colour to that of urine. Analyzed by Gmelin and Peschier, they give the percentage of tannin as 38·3 and 42·6. Little is known of it in England.

Extracts.—*Kino*, *Gum Kino* (*Pterocarpus marsupium* and *Drepanocarpus senegalensis*), is imported from the East Indies, Australia, and Madagascar. It contains 75 per cent. of tannin, being one of the richest agents with which we are as yet acquainted. Its great price has prevented its use in tanning, being principally employed for medical purposes.

Catechu (*Acacia catechu* and *Uncaria gambir*) is another dried extract; it is met with in commerce in a variety of forms, and known as *Terra Japonica*, *Gambier*, and *Cutch*. A comparatively small quantity of cake catechu is imported in the form of circular cakes, 5 to 6 ozs. in weight. This is said to be obtained from the *Acacia catechu*. Dr. Hooker, in his "Himalayan Journal," states, "This province (Soane Valley) is famous for the quantity of catechu its dry forests yield. The plant *Acacia catechu* is a little thorny tree, erect, and bearing a rounded head of well-remembered prickly branches; its wood is yellow, with a dark brick-red heart, most profitable in January for yielding extracts." It is exported from Bombay and Bengal. The great proportion of it is consumed by dyers. The *Uncaria gambir*, a shrub growing from 6 to 8 feet in height, is the great source from which our supply of gambier is procured. It abounds in Malacca, Rhio, on the island of Bintang, about thirty miles from Singapore, which is the principal port of export. The planters grow it in connection with pepper, as the refuse of the gambier forms an excellent manure for the pepper plant. The average quantity exported from Singapore for seventeen years, up to 1875, was 25,279 tons; and to show the rapid development of the trade, it is only sufficient to place before the reader the actual imports of the same into England. In 1824, 4 tons 9 cwts. was the amount of import; in—

1860,.....	9.964 tons.
1863,.....	12,064 "
1870,.....	20.600 "
1875,.....	20,877 "

But Singapore exported altogether in 1875 36,717 tons, the largest export of which we have read.

The gambier is exported from Singapore in two forms: the largest proportion is in large blocks, weighing about 2 cwts. From the facility with which other things can be mixed with it, it is generally adulterated, or rather weighted with earth and rubbish, often very damp. The other kind is made into pieces of a cubic inch, quite dry, and readily breaking, showing a yellowish colour, with a tinge of red. This variety is known as cube gambier. Occasionally another variety, known as *pressed cubes*, is to be met with in the market, which is identical with the last; but when nearly dry the cubes are pressed into larger bales, and thus in transit often get heated, and their colour thereby much deteriorated. The natives prepare the best cube gambier in the following manner:—The leaves and small branches are collected three or four times a year. They are thrown into a large cauldron, the bottom of which is of iron, the upper part of bark; water is supplied to the cauldron (would not boiling in vacuum pans be better?); its contents are boiled for five or six hours, until a strong decoction is obtained. The leaves are then withdrawn, and allowed to drain over the vessel, which is kept heated for as many hours, until the contents are inspissated; allowed to cool, the catechu subsides; the water is drawn off, and a soft soapy substance remains, which is cut into small cubes about an inch square; these are laid on frames to dry. During the process of boiling, a certain quantity of starch or farina is thrown into the mass to help to consolidate it.

The common block gambier gives about 42 per cent. of tannin.

On the introduction of gambier to England some fifty years since, the dark red colour which it imparted to the leather gave it a bad name, and for years it was neglected; but the removal of the tax from leather, and its increased consumption, led to many attempts to use it — its richness in tannin being a great inducement to employ it for the manufacture of leather. F. CHAPLIN took out a patent for its use in 1836, in which gambier was exclusively used. The hides being sewn together at the edges, strong terra liquor was forced into the bag through a hole left in the neck; the hydrostatic pressure thus excited forced the liquor through the pores of the hide, very rapidly tanning it. The market was flooded with this cheap leather; but the bad colour, combined with its very inferior quality, brought it into disgrace. The patent became a dead letter. It is well to remark that although the percentage of tannin in gambier is large, the chemical combination between the tannic acid and the gelatinous fibre of the hide does not appear to be thorough, as with most other agents. It is not perfectly insoluble, as repeated immersions in hot water will remove nearly all the tannin from the skin. The analysis of gambier gives—

Tannic acid,	48·65
Catechuic acid,	37·25
Gum,	6·09
Insoluble,	7·02
	100 00

Catechuic acid, it will be observed, is one of the constituents. This acid imparts the objectionable red colour to the infusion; and it is ascertained in working in the tan-yard that gambier slowly dissolved in cold is free from catechuic acid, but when heat is applied the catechuic acid is dissolved, and a bad colour the result. This statement as to the colour of catechuic acid is doubtful. When first employed in tanning, it was used in large quantities without admixture with other agents, as rapidity in the process was the desired end. It is now more advantageously used in various proportions at different stages of the process; but the quantities given are small. Treated in this manner, its use is of considerable advantage; especially is this observed in the manufacture of light leather, for which it appears admirably adapted, giving a soft mellow character to the leather; if not used in excess, the colour also is good. Large quantities of block gambier are consumed annually in the tanning of East India kips, which, being naturally intractable in the manufacture, require that the tanning material employed should be soft and mellow in its action; this is obtained by a mixed tannage of gambier and valonia.

Hemlock Extract (*Abies canadensis*).—The hemlock spruce fir, an evergreen, rising to the height of 70 to 80 feet, abounds in the United States and Canada, and is said to form three-fourths of the woods of the Northern States. The bark is commonly employed by the tanners in their several localities. Within the last fifteen years an inspissated extract has been prepared in Canada, which is shipped to our market in large and increasing quantities. It arrives here in casks, about the consistency of treacle, of a dark red-brown colour by transmitted light. Messrs. J. & J. MILLER & Co., of Upton in Canada, took out a patent for the preparation of hemlock extract in 1864, and up to the present time are the principal shippers of it to our shores. Although great prejudice existed against it because of its colour, and the large amount of resinous matter it held in solution, yet the trade has increased; and the manufacture is said to be carried to a greater perfection, the import for 1875 being about 6000 tons. The extract is insoluble in cold water, but dissolves readily at a temperature of 150° Fahr. Like many other novelties in the trade, when introduced it was employed too exclusively, giving a bad colour to the leather; it is now, however, used as a useful adjunct to other materials. According to RAMSPACKER, it gives 25 per cent. of tannin.

Chestnut Extract is quite a recent importation. It is much more liquid than hemlock extract, of a dark colour; it contains 18·5 per cent. of tannin.

GALLS are excrescences of the *Quercus infectoria*, and also the other kind known as *Knoppern*, obtained from the *Quercus pedunculata* and *Q. pubescens*. The latter are especially the growth of Austria and Hungary, also of Piedmont; they are exported from Trieste, and contain 25 per cent. of tannin. Galls are the abnormal growth of the oak, which at certain seasons may be seen very abundant on the twigs and stems of our English oaks. The puncture of the bark by a small fly (*Cynips Quercus folii*), which thus seeks to find a resting-place for the eggs, depositing at the same time a drop of acid liquid, which sets up a state of inflammation resulting in the arrest of the sap and ultimate growth of the gall. The centre of gall contains the grub, which when arrived at maturity eats its way through to the open air, and commences life on its own account.

The galls of the English oak have never been employed for tanning. The eastern shores of the Mediterranean supply the great bulk of the agent. The oak known as *Quercus infectoria* is the main source from which the Aleppo market is supplied. Previous to the gathering, the progress of the galls to maturity is carefully watched, as the great point to be desired is to secure the gall when it has attained its proper weight, before the exit of the insect. Galls thus obtained are termed *green galls;* but the galls from which the insect has flown are called *white galls*, being deficient in weight and tannin, and easily recognised by the small aperture through which the insect, *Cynips galliæ tinctoria*, has escaped.

France also furnishes galls; but as yet they cannot be termed an article of commerce, the supply being limited, and inferior to the Turkish. Galls are in use for dyeing, as also for the manufacture of ink; only very occasionally have they been available for tanning. MÜLLER'S analysis shows that they contain up to 77 per cent. of tannin.

Tamarix Galls.—*Tamarix indica* and *T. africana* are the small galls found on the tamarisk plant, about the size of a pea. In India they are known by the natives as *Sumrut ul tooria*. They appear to be used medicinally in that country, and occasionally small quantities reach England. When better known, and their tanning properties more fully recognized, they will be cultivated more extensively. These galls contain 50 per cent. of the purest tannin with which we are acquainted. *T. africana* is exported from Algiers, being the growth of Morocco.

Leaves.—*Sumach* (*Rhus coriaria* and *R. cotinus*) is the powdered leaves and twigs of the Venus sumach, or wild olive, and the elm-leaved sumach. The plants are widely spread, being found in the south of Europe, Asia, and United States. Dyers are the principal consumers of the sumach obtained from the *Rhus cotinus*. *Rhus coriaria* grows to the height of 8 to 12 feet. It is found wild in all the countries bordering the Mediterranean, Spain, France, and Italy, producing sumachs of different values. Sicily supplies the best. Palermo sumach is of world-wide celebrity. In 1873 there were fifteen steam mills at Palermo for grinding sumach, and the trade is rapidly increasing. The quantity exported from Sicily in 1842 was 123,305 tons. Imports into England, 1840, 9351 tons; 1845, 11,398 tons; 1850, 12,929 tons; 1870, 14,431 tons.

Sumach comes to England generally in bags weighing 1½ cwt., marked with the brand of the maker, the colour being yellow with a slight tinge of green. Good sumach gives 17 to 18 per cent. of tannin. The branches are collected when the foliage is at the best; the leaves are separated, dried, and finally ground under millstones. Whilst the grinding enables the maker to forward the sumach in a compact form, it gives the opportunity for adulteration, which in a few cases, as the value of the article has risen, has been used by unscrupulous dealers to their own advantage. A species of flags grows in the marshes of the district; when dried and ground its powder bears a great resemblance to sumach. For the purposes of adulteration it has been so employed, as small quantities of the clayey soil containing iron adhere to the roots of the flags, and are ground with it. The fraud is detected by the tanner, by the dark spots left on the leather when brought into contact with the gallic acid of the liquor. The especial characteristic for which sumach is valued is, not so much for the strength of its tannin, but rather for its capability of working with other tanning materials, either at the same time or afterwards, imparting a good fawn-like colour, also great softness and mellowness, to leather. For this purpose it is largely used by tanners and curriers for qualifying leather, which without it would work hard and intractable. Sumach is remarkable for the readiness with which its tannic acid becomes changed into gallic, especially when the solutions are warm. The return of such liquors to the brewing taps brings it in contact with other tanning materials; a kind of fermentation is originated, known in the trade as souring of the liquors, and great loss of tannic acid ensues. Professor Calvert, in his experiments on sumach and other materials, asserts that he has discovered two substances which possess the property of arresting fermentation in tanning extracts. They are—bichloride of mercury, and, especially, carbolic acid. The latter is the only one which the tanner may safely employ, as not being detrimental to his liquors. There are doubtless other things which may be applied, and chemists are endeavouring to obtain some substance which shall be both cheap and efficacious when used on a large scale. H. R. Proctor has placed before the trade a new compound, which he calls *Antigalline*, which entirely prevents the formation of gallic acid.

Fruits.—Valonia, the pericarp or acorn cup of the *Quercus ægilops*, growing on the highlands of the Morea, Roumelia, Grecian Archipelago, Asia Minor, and Palestine. Although it receives its name from Vallona, a town of Albania, and considerable quantities are shipped from Greece, yet fully three-fourths of the crop is exported from Smyrna. For some years the export has been nearly the same. The following table will show the exports from Smyrna to the United Kingdom:—

	Quintals.		Quintals.
1856	376.000	1864	373.000
1857	426.000	1865	309.000
1858	364.000	1866	459.000
1859	452.000	1867	334.000
1860	326.000	1868	459,000
1861	311.000	1869	415,000
1862	507.000	1870	421,090
1863	594,000	1871	501,000

From *Tanner's Journal*, Dec., 1872. 1 Quintal = about 1 cwt.

The imports into England for 1875 were 23,299 tons, but considerably damaged by honey dew. The tree from which the acorn is gathered is scattered over hundreds of square miles. Dr. Hooker, writing of it, says, "It rises on a stout gnarled trunk, from 1 to 2 yards in circumference, to the height of 20 to 30 feet, a rather round-headed, densely leafy tree, giving an open park-like appearance to the landscape." The quality of the valonia, and the size and shape of the pericarp, vary considerably, according to the locality from which it is obtained; certain districts, such as Aidin, Borlo, Demergick, standing in good repute. A good sample should be composed of medium-sized cups, the rim or wall of the pericarp very thick, with the exterior spines small and uniform in size. The cup, being cut or broken, should give a bright drab fracture. The fruit ripens in July and August, when the trees are beaten, the acorns remaining on the ground to dry. The natives gather them from the ground and transport them on the backs of camels to the stores in the towns; or they are conveyed by camel and train to Smyrna, where are large and airy stores, in which the bulk is allowed to lie in heaps about 5 to 6 feet in height for some weeks; during which the mass heats, the acorn itself, which contains no tannin, contracts, and readily falls from the cup. This process of incipient fermentation is attended with considerable risk; if carried too far, a large proportion of the bulk becomes dark in colour, and other-

wise damaged. When ready for shipment the heaps are picked over by hand; the best cups being reserved as *Trieste* for the Austrian market, the remainder going as *English*. In some cases, the rubbish having been removed, the remainder passes under the name of *natural*, and is thus exported to England. Another variety, called *camatina* (being the smaller cups gathered before becoming ripe), is principally used by dyers; 25,000 tons appears to be the average for many years, and although the demand has increased year by year, the supply has remained stationary. The two oaks to which we are indebted for our supply of galls and valonia, *Quercus infectoria* and *Q. ægilops*, grow side by side over the large proportion of Asiatic Turkey, so that with a little attention the crop of both could be trebled. But the insecurity of life and property prevents the development of the trade. Now and then the pericarp is attacked with a kind of honey dew, which deposits on the cup, and makes it very liable to heat when gathered, the cup becoming very dark and deficient in tannin. The crop of 1875 was considerably damaged from this cause, many parcels reaching England in an unsaleable condition. The cause of the disease has yet to be ascertained; when the cup is large and the acorn fully developed, the disease appears specially liable to appear. Valonia is valued by the tanner, because it imparts to the leather firmness and weight. When used alone, the leather becomes too hard and brittle for general purposes; it therefore is almost invariably mixed with oak bark or other agents, such as myrabolans and mimosa. A good sample of valonia yields 26 to 32 per cent. of tannin. Valonia deposits a large quantity of *bloom*, or ellagic acid. The tannin appears to differ from that of galls, as it affords no pyrogallic acid on destructive distillation. Dr. Stenhouse found only a trace of gallic acid in this material.

Myrabolans (*Terminalia cherbula*), are obtained in India from a small tree allied to the myrtle. The dried fruit of the tree, about the size of a small date, contains a hard stone in the centre; the whole of the tannic acid is contained in the pulp enveloping the stone. Our present knowledge of the plant is small. It appears to abound in India, and any quantity might be collected if attention were directed to its cultivation. Myrabolans are exported from the three presidencies, the fruit from each differing very essentially in appearance and tanning properties. Professor Bernardin speaks of three or four kinds, such as *Terminalia angustifolia*, *T. bellerica*, *T. citrinum*, *T. tomentosa*, which may account for the variety in which they are to be found in the market. Some are small, wrinkled, and of a yellowish colour; others are larger, round, and of a darker hue. The latter appear to have been gathered when dead ripe, and are therefore deficient in tannin. A good sample of myrabolans will give as much as 40 per cent. of tannic acid. Import into England, 1867, 64,243 cwts.; 1874, 11,230 tons; 1875, 9,800 tons. The growth of the supply has been rapid, and is still on the increase. Myrabolans deposit a large amount of *bloom* or *ellagic acid*. During the process of tanning they yield a considerable amount of acetic and gallic acids, and would be invaluable to the tanner, were it not that they make leather soft, and have not such weight-giving properties as valonia.

Divi Divi (*Cæsalpinia coriaria*), belonging to the *Leguminosæ* or pea tribe, is the pod of a tree indigenous to the northern shores of South America—Rio Hache, Maracaibo, and Savanilla being the ports from which it is shipped. The tree grows to the height of 20 to 30 feet; the pods are of a dark brown colour, and twisted during desiccation to the shape of the letter S. The whole of the tannin appears to reside in the yellow pulp, just beneath the rind, the taste of which is very astringent and bitter. Dr. Stenhouse informs us that whilst the tannic acid of divi divi is similar to that of galls in its reactions with salts of iron, yet it differs from the latter, as it does not yield pyrogallic acid. The infusions during the process deposit a large amount of *bloom*. Divi, like sumach, when exposed to the air very rapidly undergoes a kind of fermentation, so that the liquor assumes a dark red colour; the sides of the pits also are stained a similar hue. By sudden changes of the temperature the infusions are especially liable to be affected; the mucilage of the pulp, with the organic oil of the seed, tend to produce the fermentation. The process carried on in closed pits, so as to exclude the air, produces leather of a better colour. Divi divi gives great weight compared with other materials, but the leather is generally of a darker hue. It also imparts to the leather a horny feeling in dry weather, with a great affinity for damp in wet weather. Austria, Poland, and Silesia consumed the greater portion of the crop up to the year 1873; but the evident superiority of the English leather shown at the Vienna Exhibition led them to turn their attention more to valonia. In 1875, when valonia rose to £30 per ton, many English tanners had recourse to divi, but as speedily relinquished its use when valonia receded to its original value. The best divi divi contains 56 per cent. of tannin.

Balsamocarpum brevifolium, a kind of bean growing in the mountainous districts of Chili, South America, is mentioned here not as being in general use; but as attempts are being made to cultivate it more extensively, it is hoped that it may rank among the reliable supplies in a short time. The high price of the principal tanning agents in 1875 kept the matter of future supplies before the public; the world was ransacked for other materials; balsamocarpum was thus introduced to notice through M. Ramspacker of Paris. It appears to differ from other agents in being a gum of great strength, and very rapid in its action. The whole structure of the bean, with the exception of the seed, appears to be full of tannin. It yields 80 per cent of tannic acid. It is very soluble in water, and is therefore gathered before the rains, as otherwise the fruit is washed to the ground, and found in quantities mixed with the soil; in this condition some small parcels have reached England, the pod itself being of so fragile a character that it has only been exhibited as a novelty. Strenuous efforts are, however, being

made to promote its cultivation in climates adapted to its growth. The tannin of balsamocarpum changes very rapidly into gallic acid; so rapid is the decomposition that, to secure the full benefit of the tannic acid, the infusion has to be applied directly to the leather. The usual mode of proceeding is to supply small quantities to other ingredients after the leather has been some time in tan.

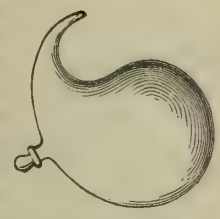
Testing of Tanning Materials.—Not only is it necessary for the tanner to know the number and character of the agents with which he may have to deal in his trade, but also to know how practically to test the value of these different agents. Whilst oak bark was the staple material employed, a little practice was sufficient to enable him to speak with confidence as to its quality. The colour of the bark when broken, with the amount of epidermis, would generally guide him; or the colour of the infusion, with the taste, would be all that was required to pass judgment on a sample of bark. The case is altogether different now. The markets afford the tanner the opportunity of purchasing a variety of tanning materials, much stronger in tannin, with greater rapidity of action. A demand has therefore arisen for some definite and reliable method for estimating the amount of tannic acid in each substance. The first step towards this has been the estimation of the specific gravity of the infusions. This has brought into use the hydrometer, or rather barcrometer, an instrument very commonly employed in English tan-yards. Chemists obtain the same results, with more accuracy, by the specific gravity bottle. This is, at best, but a rude method of estimating the amount of tannin. It soon became apparent that the barcrometer simply gave the density of the infusion—nothing more. It did not follow that the increased density showed, *pro rata*, the same increase of tanning properties; especially was this apparent when a new material had to be dealt with, which perhaps contained some amount of extractive matter, or mucilage. Also, an old and nearly-spent infusion, containing some quantity of gallic and acetic acids, and probably lime and rubbish, would register much higher than its real worth.

Fig. 6.



Various modes of analyzing tanning materials are now in use, of which a brief description will be appropriate here. Davy, Stephens, Warrington, Müller, Stenhouse, and Galloway have each added to our knowledge in this matter. Stephens employed thin strips of dried skin, previously weighed, which were soaked in clean water, and then suspended in a vessel containing a weak infusion of the tanning material; after it had abstracted all the tannic acid, the skin was dried and weighed, the difference between the two weights showing the amount of tannic acid imbibed. This was a tedious process, and great difficulty was experienced in removing the whole of the moisture of the skin. Sir H. Davy threw down a precipitate of tannic acid with warm solution of gelatine, weighing the precipitated tannogelatine. This also involved the drying of the precipitate, which has been an objection to its use. Lowenthal's method of volumetric analysis, based on the oxidation of solution of indigo by permanganate of potash, is a very delicate and beautiful experiment; but the quantities analyzed are very minute, and the presence of other organic bodies interferes with the reaction. The process is altogether an elaborate affair, involving a knowledge of chemistry considerably beyond the attainments of many in the trade. Warrington and Müller obtain the same result by preparing a standard solution of gelatine—300 grains to 20 ozs. of water; to this Müller adds 75 grains of alum. This is carefully prepared by allowing the gelatine to soak in 10 ozs. of cold water for twelve hours; the bottle with gelatine is then placed in warm water, and gradually raised to 212°, when the solution of alum is added, and the whole solution made up to 20 ozs. After being well mixed, the solution is placed back to cool. In analyzing the solution is warmed, then placed in one of Schuster's *alkalimeters*, the stopper inserted, and the whole weighed. The solution, after weighing, is carefully applied to a prepared infusion of the tanning material; during the operation the infusion in the beaker is stirred with a glass rod, when the whole of the tannin is precipitated; the alkalimeter with the residue of gelatine is re-weighed — 155 grains of gelatine solution = 5 grains of tannic acid. Very correct results are obtained by this process, if care is taken not to apply an excess of gelatine. The precipitate therefore should be allowed to settle now and then. A few drops of the pure supernatant liquor should be placed in a watch glass, to which a drop of gelatine may be added, and thus the point of saturation readily ascertained. Galloway's students, at the museum of Irish industry, have obtained very accurate results by this process, as may be seen in a paper read at the British Association, Aberdeen, 1859, a copy of which is given here; to these are added a few analyses furnished by others:—

Fig. 7.



	Per Cent.	Authority.
Oak bark, 100 years old,	8·45	Müller.
" young,	13·87	"
" British, 50 years old,	8·90	Mulligan & Dowling.
" " about 50 years,	9·76	"
" " about 70 "	6·12	"
" Southampton, 50 "	8·30	"
" coppice, picked sample,	12·35	"
" Irish, picked sample, 45 years,	9·50	"
" Belgian popering,	8·33	"
" " heavy coppice, picked sample,	10·74	"
" Belgian, light,	8·52	"
" Esching,	19·35	G. Müller.
Mimosa bark,	17·97	Mulligan & Dowling.
"	31·16	G. Müller

	Per. Cent.	Authority.
Mimosa bark,	27·92	W. N Evans.
Willow bark,	3·95	Mulligan & Dowling.
" Leicester,	6·80	Davy.
" weeping,	16·40	Cadet de Gassincourt.
Larch bark,	3·51	Mulligan & Dowling.
Cork tree bark,	12·16	"
"	12·53	W. N. Evans.
Hemlock bark,	13·92	Mulligan & Dowling.
Divi divi, inferior,	29·80	"
"	49·25	G. Müller.
Valonia, Smyrna,	34·78	Mulligan & Dowling.
" "	32·25	W. N. Evans.
" " honey dewed,	22·00	"
" Camatina,	26·00	"
" Greek,	22·00	"
Myrabolans.	20·91	Mulligan & Dowling.
" good sample,	35·08	W. N. Evans.
" pulp, without stones,	55·76	"
" stones, after washing and drying,	4·02	"
Sumach.	19·35	G. Müller.
" Palermo,	24·37	Mulligan & Dowling.
" Malaga,	10·40	Frank.
" Virginian,	10·00	Cadet de Gassincourt.
Catechu, Bombay, light colour,	26·32	Mulligan & Dowling.
" " "	55·00	Davy.
" Pegu (cutch?), dark brown,	46·88	Mulligan & Dowling.
" Bengal,	44·00	Davy.
Mangrove bark,	28·00	W. G. Fry.
"	17·21	W. N. Evans.
Tormentil root,	46·00	Cadet.
Balsamocarpum,	50·00	J. Watts.
Hemlock extract,	25·00	"

Hammer estimates tannic acid by the use of fine shreds of dried skin, in a method somewhat analogous to that of Stephens' strips of hide, and open to the same objection.

In the previous mention of different methods for analyzing tanning materials given in this paper, notice was taken of Löwenthal's process; but an opinion was expressed that the process was too elaborate for general use—that the system of analysis, though a beautiful experiment, was more adapted for the lecture room than for practical purposes. Since this was written Löwenthal has made an addition to the course of analysis, which it is thought desirable should be placed before the reader, as now giving the most accurate results. The following solutions must be made:—

1st. 4 grams. pure permanganate of potash in 3 litres of *good water* (that is, water free from contamination with organic matter; distilled water, or what is called such, obtained from the condensed steam which has passed through the engine, contains grease and oil; rain water is seldom pure; good drinking water will do).

2nd. 5 grams. of pure precipitated indigo in 1 litre of water.

3rd. Dilute sulphuric acid (1 to 3 of water).

4th. 25 grams. of good transparent gelatine, well swollen in cold water, then dissolved by the aid of heat. The solution is made up to a litre, and saturated with pure table salt.

5th. A saturated solution of pure salt, containing 25 c.c. of sulphuric, or 50 c.c. of hydrochloric acid per litre.

To make an analysis, 10 grams. sumach, or 20 to 25 of bark, are exhausted by boiling with water, and the solution when cold made up to a litre. Of this infusion 10 c.c. are mixed with three-quarters of a litre of good water; 25 c.c. of the indigo solution and 10 c.c. of the dilute sulphuric acid are added. The permanganate solution is run drop by drop from the burette, with *constant* stirring, till the deep blue of the indigo changes to a clear yellow, and the moment this takes place note the quantity of permanganate used; call this quantity A. Next repeat the same process with the indigo and sulphuric acid alone; call the quantity B. Substracting B from A, the amount of permanganate is obtained which was required to destroy the total astringents of 10 c.c. of the tannin infusion. The permanganate acts as an oxidising agent, consuming both the tannin and the indigo. As the tannin is the more readily oxidised of the two, it is consumed first; and when the indigo is all bleached, we may be sure that the tannin is destroyed also. In order, however, to attain this satisfactorily, the proportion of indigo should be such as to require about twice the quantity of permanganate which would be consumed by the tannin alone. Thus, if indigo alone requires 10 c.c. of permanganate to decolorize it, the indigo and tannin together must not take more than about 15 c.c.; and if it does so, the tannin infusion must be diluted accordingly, or a less quantity employed.

The next step is to ascertain the proportion of gallic acid and impurities in the sample. 100 c.c. of the tannin infusion are mixed with 50 c.c. of the salted gelatine solution; then, after well stirring, add 100 c.c. of the salt and acid solution, and leave the mixture all night; then filter, and the filtrate should be completely clear. Now test 50 c.c. of this filtrate with permanganate and indigo as before; thus will be obtained the amount of permanganate required for the gallic acid and impurities alone, the gelatine having entirely precipitated all the tannin previously. To make the working clearer, an example is given of one of Löwenthal's papers:—

10 grams. of sumach were boiled in three-quarters of a litre of water, and after cooling made up to 1 litre.

		Permanganate c.c.
(1) 10 c.c. sumach infusion, 25 c.c. indigo solution	consumed	16·6
Ditto repeated,		16·5
		33·1
50 c.c. indigo solution alone,		13·2
Total permanganate for 20 c.c. sumach,		19·9

		Permanganate c.c.
(2) 50 c.c. filtrate from the gelatine, 25 c.c. indigo solution	consumed	11·2
Ditto repeated,		11·1
50 c.c. indigo alone,		13·2
Gallic acid and impurities,		9·1

Deducting 9·1 c.c. from 19·9 c.c., 10·8 c.c. is the remainder, as permanganate equivalent to the tannin of 20 c.c. of sumach infusion, or 0·2 grams. of dry sumach.—*Tanners' Journal*, March, 1877.

This process gives accurate results; and although it may appear complicated, it may be readily accomplished by any one after one or two trials. Many tanners use Lowenthal's method with success.

Another process, preferred by some chemists, is the cupric acetate method. To the solution of tannin add saturated solution of cupric acetate till the supernatant liquor is blue: then add excess of solution of ammonic carbonate; wash once by decantation, and then rapidly filter in a vacuum, dry at 100° C., and weigh—1·3 gram. equal to 1 gram. of gallo-tannic acid; the composition of the precipitate is adapted for valonia, oak bark, and myrabolans.

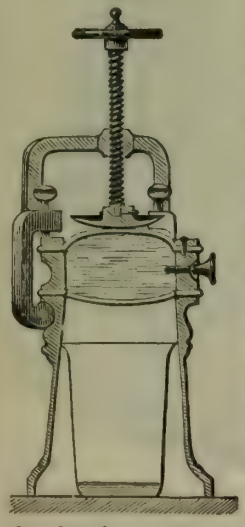
Gerland's Antimonial Process, which can be applied to gambier and divi divi. This is volumetric. The quantities are as follows:—2·611 grams. of tartrate of antimony dried at 100° C. are dissolved in a litre of water; 1 c.c. of this solution = 0·005 grams. of tannin; a few drops of saturated solution of chloride of ammonium is found to help precipitation. This process gives good results, but it is seldom employed, because the solution is liable to decomposition.

Ferricyanide of Potassium Process.—This includes the use of a standard solution of plumbic acetate. The acetate of lead is allowed to drop from a burette into a solution of tannin; the precipitate which results is of a white colour until the whole of the tannic acid has been neutralized, which is evidenced by the appearance of a red tinge to the solution on the addition of ferricyanide of potassium. The proportions are as follows:—

Acetate of lead,	2½ grams.
Water,	½ litre.
The Indicator—	
Ferricyanide of potassium,	5 milligrams.
Strong ammonia,	5 c.c.
Water,	5 c.c.

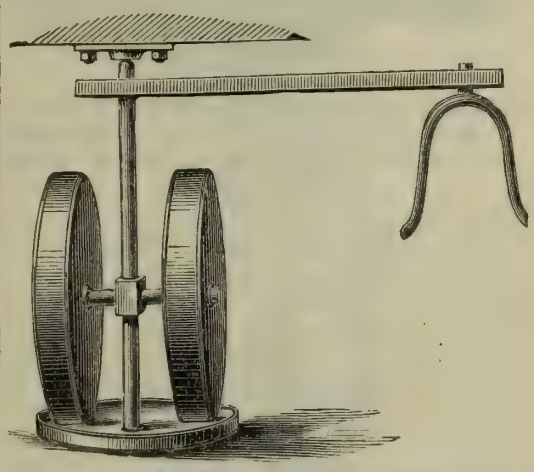
Before using, the lead solution must be diluted with 9 times its volume of water, having previously been standardized with pure tannic acid. A small apparatus has been lately brought before the notice of the trade, the joint invention of two Frenchmen, Messrs. Muntz and Ramspacker, Fig. 8. It is composed of two parts, the lower forming the base, on which a piece of prepared skin is laid. The upper portion, fitted with a long screw, when in use is fixed on to the lower by screw clamps, and the machine is ready for use. The space between the piece of skin and the India rubber dome is just sufficient to contain 100 c.c. of the tanning infusion, which infusion, previous to being placed in the machine, is tested by a small hydrometer to ascertain its specific gravity. When the infusion is placed in the machine, and the brass plug screwed tight at the side, pressure is brought to bear on the dome, and there being no means of egress for the liquor it has to pass through the pores of the skin; all the tannin is abstracted by the gelatine of the pelt; clean water, or water containing gallic acid, is collected in the glass below. This water is again tested with the hydrometer, the difference between the two specific gravities, with a little calculation, showing the percentage of tannic acid. This machine, or tan-tester, as it is called, has proved of great value at the present time; its simplicity, and the rapidity with which the operation can be performed, has led to its general adoption, not only in England, but also on the Continent. Its use has modified considerably the estimation of value of many tanning agents. As it gives not only the amount of tannic acid, but also of all that goes to make leather, it in fact brings the tanyard into a nutshell; and before his own eyes the tanner is able in half an hour to partially tan a piece of skin, and in this manner practically to reveal the tanning properties of the material. It is not to be wondered that its success has produced much adverse criticism. But it can and will survive all this.

Fig. 8.



Machinery for Grinding.—It is important that the different barks and other materials should be crushed and disintegrated, to facilitate the more rapid abstraction of the tannin. In grinding barks and kindred substances, which possess a fibrous texture, the end to be desired is to crush the fibre, and at

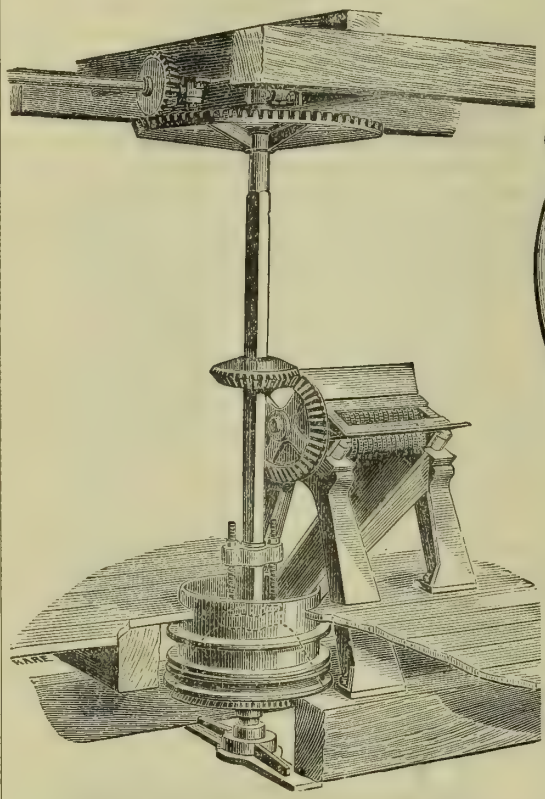
Fig. 9



the same time drag away every fibre separately from the next; the aim of the millwright should be to reduce the bark to a condition much resembling rag tobacco, a mass of crushed fibres, with but little dust. This process is termed *ragging*. Many mills will reduce to powder, but do not rag. In some secluded parts of Devon and Somerset were to be seen a few years since tolerably perfect specimens of the bark mills of our forefathers (Fig. 9); two large circular stones set on edge, revolved not only on their own axes, but partook also of a circular motion, imparted by connection with the upright shaft. The

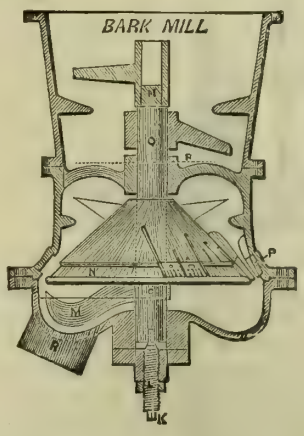
bed on which they revolved was generally a large basin formed out of one granite stone; the bark was not only crushed, but a slow grinding was also

Fig 10.



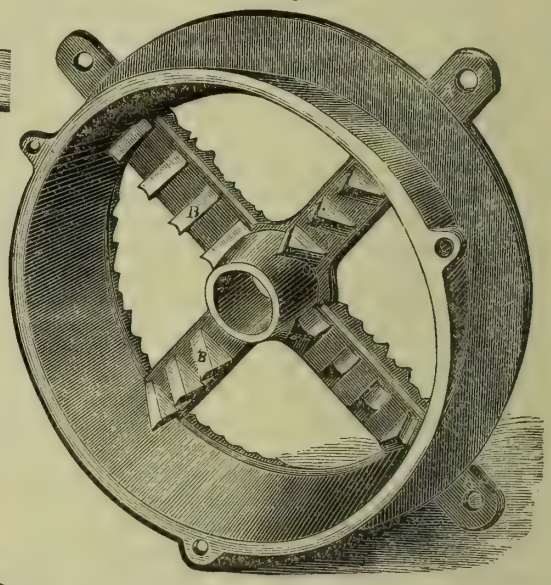
effected. The work was tedious in the extreme. In fine weather, with the bark dry, excellent work was accomplished, the bark being well ragged; but

Fig. 11.



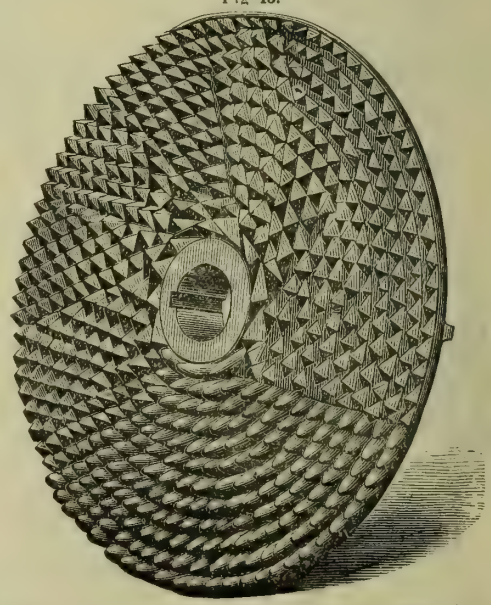
with the atmosphere in a humid condition no progress could be made. The improved mills of modern days are constructed on the same principle as the coffee mills, only vertical, and adapted to the grinding of tons rather than lbs. The mills of Taylor and Bodley, and Huxcham and Brown, of Exeter (Fig. 10), are deservedly held in repute for simplicity in construc-

Fig. 12.



tion and excellence of work; they are generally supplied with breakers, B, which cut the bark in convenient lengths for the mill. They are used also for the grinding of valonia. In giving a sketch of the Exeter mills, two American mills are also given (Figs. 11, 12, 13, 14), one made by Mosser, of which Mr. J. Schultz,

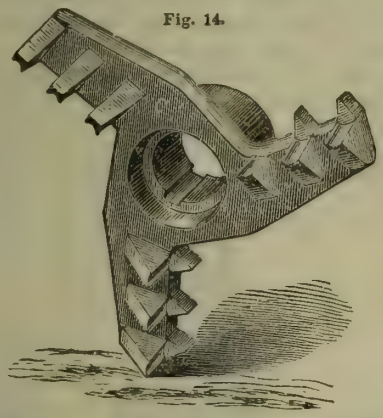
Fig. 13.



of New York, speaks very favourably. But the advent of mimosa, which requires to be ground very fine to extract all its tannin, and myrabolans, with its hard stone, necessitated mills of a different construction.

Both of these materials are very hard, and are brought to condition of powder. In the beautiful cemetery of Arno's Vale, near Bristol, may be seen the modest stone bearing the name of Thomas Carr, M.T.M.E., who died March 29, 1874. Below the name, cut out of the solid marble, is the model of the working interior of the first disintegrator. The inventor who gave birth to the idea, like

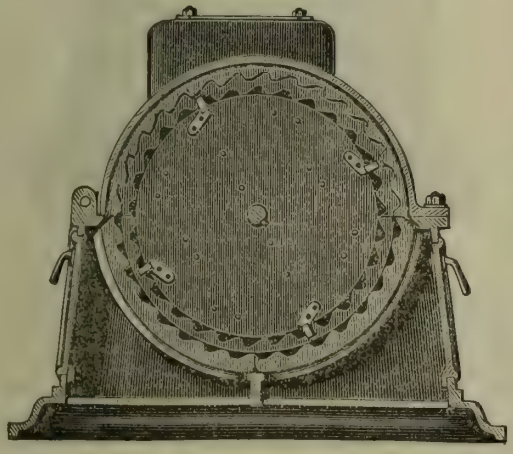
Fig. 14.



many others, never lived to reap the full reward of his ingenuity. Instead of 20 revolutions per minute, as most mills revolve, Carr conceived the idea of driving a mill of simple construction at a very great speed, namely, 1500 revolutions per minute. It was not a grinding process, but one in which the material operated on was knocked or battered to pieces.

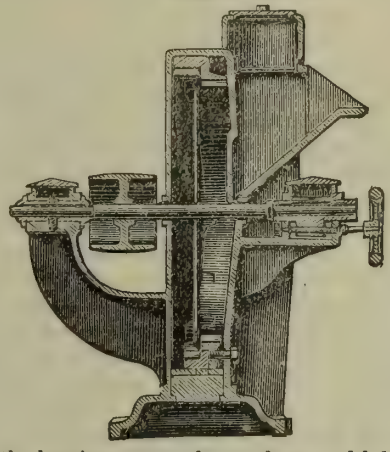
Others have improved on the construction of these machines. Wilson's universal disintegrator, of which

Fig. 15.



a sketch is given, is driven at the speed of 3000 revolutions per minute. The inventor states that this mill grinds every description of tanning materials—oak bark, mimosa, valonia, and myrabolans, also a great variety of material for other trades. The reason it is able to accomplish such a variety of work is due to the principle on which it works, namely, percussion, or, in other words, beating the material to atoms by reiterated blows of several steel beaters driven at a high velocity, which is effected in the following manner. Inclosed within a circular casing or drum is a rapidly rotating steel disc, with several steel beaters rivetted on each side; this disc answers the purpose of a fly wheel, dividing the casing into two compartments, which are serrated on their internal peripheries; the first compartment being a little smaller than the second, the disc in the second compartment is larger than the first. The material which is required to be ground is fed into the first compartment through the hopper, and coming into contact with the beaters on the rotary disc, is, by the rapid action thereof, dashed against projections or breakers on the casing, or against the serrated periphery. The action is continued until the particles are reduced sufficiently to pass the serrated periphery of the first compartment and the edge of the disc into the second compartment. They are there subjected to a further beating or reducing action, and pass away through the discharge aperture forming the whole of the bottom of the second compartment. With regard to wear and

Fig. 16.



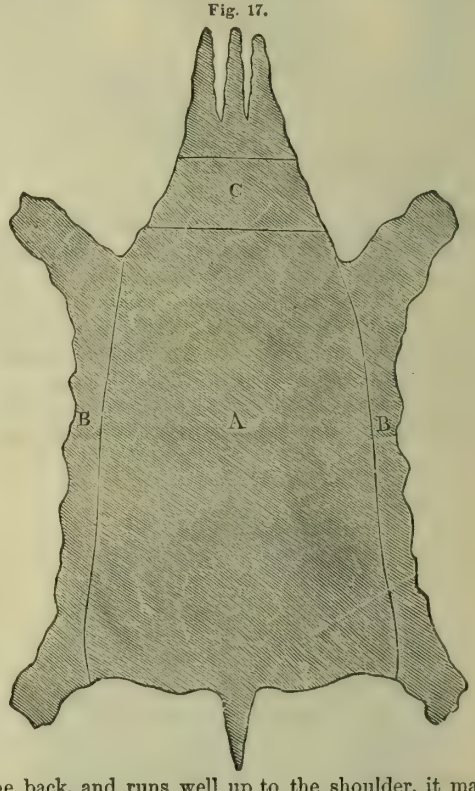
tear, the bearings are made very long, and lubricated with tallow. There are no cutting edges to sharpen, the beaters being blunt pieces of steel hardened on the face. The mill is constructed in two halves hinged together at the end, and fastened with bolts, so that it can be readily opened for repairs. The disc is very strong and light, and forms a fly-wheel with little resistance to the air; one advantage of the mill being the fact, that it will pulverize the material either dry or wet.

Hides and Skins.—The skins of all animals are capable of being transformed into leather; but the number of those with which the tanner has to do are comparatively limited. The ox, horse, sheep, goat, pig, and seal, are the principal.

Ox hides occupy the most prominent position. They are met with in the home market weighing from 60 to 120 lbs.; cow hides weigh from 40 to 80 lbs.; kips, which are the skins of young oxen previous to the horns, average about 20 to 22 lbs.; calf skins, from 4 to 18 lbs. P. L. Simmonds estimates our home slaughter at four millions, and calf skins at

half a million. No very reliable statistics are obtainable on the subject. Our supplies are drawn from all parts of the world—South America furnishing by far the largest proportion. The vast Pampas, through which the river Plate and its tributaries flow, has unlimited pastures for partially wild oxen and horses, which have been computed roughly to number nearly twenty-five millions. The large number of 3,121,758 ox hides were exported from the river Plate in 1872 to different parts of Europe and the United States. The climate and soil of the Pampas, lying between latitudes 31° and 38° south, appear especially suited to the rearing of these cattle. When this latitude is passed, and cattle are obtained from districts nearer the equator, the quality of the hide deteriorates. But on the other hand, Buenos Ayres hides, the production of the southernmost of the states, are stouter and of finer texture than Uruguay or Rio Grande. The hides from these temperate regions are salted, and exported as wet salted. But the hides obtained from tropical countries are generally dried in the sun, or salted and dried. Brazil exports largely dry-salted hides. There is a risk that in such hides decomposition may have commenced before the pelt was quite dry. To return to the home slaughter, great diversity is found within the limits of the British Isles. Hides from the north of Scotland are totally distinct in texture and substance from those obtained in the south of England. Civilization, with greater care and attention in the breeding of cattle, has produced better beef, with less bone, and hides with finer grain and texture, but the substance is materially lessened. Oxen killed in the neighbourhood of London for the Christmas markets, yield often hides of 150 lbs. in weight, almost as large as two Aberdeen hides, but very thin. For the same reason heifer hides are preferred to cows which have had two or three calves. Bull hides are looked on with disfavour, because the hide is thin in the back, but coarse and thick in the shoulder and offal. The spring may be considered the best season for the English market hides, when the hide is stout and well nourished from the stall-feeding of the winter. During late years a number of Spanish cattle have been landed in England, the hides from which are generally stouter than those obtained from our own cattle, and are quoted higher in the markets. The supply, however, is variable. At the close of the Franco-German war, a large stock of French hides, which had accumulated in Paris, were brought to England. They were of great weight, and very stout; since which time there has been a constant demand for them. The stoutest of our market hides are principally tanned as butts, or harness hides, with the best materials. The hides of lighter weights and inferior substance are tanned with various materials as common or shaved hides. Large spready hides, of sufficient substance, are now frequently passed through the splitting machine, and tanned for japan and coach-work. The best stout hides, unless required as crop or harness leather, in which case they are tanned whole, are otherwise rounded after depilation, as shown by the annexed plan:—A is the butt, which contains the stoutest and best part of the hide, suitable for sole or belt purposes. The pieces by the side, B, B, are termed bellies or offal, being thinner in substance, therefore do not require so lengthened a tanning process. The head is reserved for the glue merchant; the shoulder, C, is sometimes cut of considerable depth, the inner portion being termed a range. No definite directions can be given as to the selection of hides; experience and common sense are the best guides. A loose flabby hide will naturally give a leather of a similar character; no after process can remedy a bad pelt. When inspected at the home market, where the hides are, preparatory to sale, laid in piles doubled down, if the substance of the hide is apparently thick in

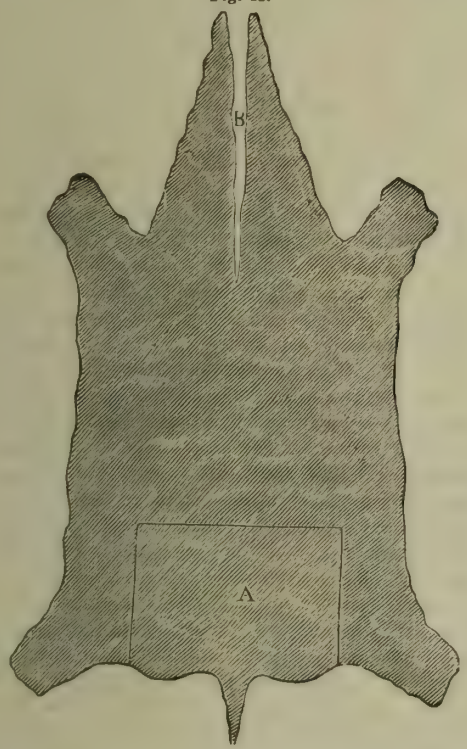
Fig. 17.



the back, and runs well up to the shoulder, it may be considered a strong, butty hide. Many hides have a weak place in the back, about 2 feet from the horns; and some are occasionally met with thin in the butt, and correspondingly thick in the offal. During the summer months care has to be taken in the purchase of home-slaughter hides, as they are then liable to *warbles;* that is, they are infested with the grub of the *Œstrus bovis*, or gad-fly, which having burrowed into the skin, when matured makes its exit, leaving a small hole, which for the time prevents the hide being used for many purposes. Salted hides from South America are brought to England in a moist condition, with salt plentifully placed between each layer of hides. They are often inspected by the purchaser as they are discharged

from the side of the vessel on to the quay, when, in order to free them from the superfluous salt, they are turned over twice before weighing, thus enabling the bystander to form an accurate judgment as to the condition and quality of the hide. These hides suffer much from branding; from two to six or seven brands are often seen on one hide, much to its detriment, as the parts thus burnt are quite useless when tanned. Efforts have been made to mark the cattle in some other less objectionable manner, but hitherto without success. It will be interesting to remember that the first cargo of salted hides imported into England were brought by Admiral Hawkins of Plymouth, who, having taken a number of slaves to St. Domingo, in 1562, invested the proceeds in hides. Dry hides from the river Plate are

Fig. 18.



mainly absorbed by the tanners of the United States and Germany, their mode of depilation being better adapted to dry hides. A dry hide of 26 lbs. would represent the equivalent of a salted hide of 60 lbs., and market hide without horns of 74 lbs.

Calf Skins—though met with in the market all the year round—are especially abundant in the early summer; in this case, also, heifer skins are preferable to steers, giving a finer grain with better substance. Salted and dry calf skins are imported in large numbers, the qualities being as diverse as the countries from which they come. Calf skins after tanning are prepared by the currier, the best for shoe work, the inferior for bookbinding. The French are deservedly celebrated for the excellence of their calf leather.

Horse Hides.—Very few good hides are brought to home markets; the majority being obtained from animals who have suffered much from neglect and hard work, the grain therefore considerably damaged. Salted South American horse hides, taken from the young wild cattle of the Pampas, are imported in thousands; they furnish the best curried leather, being thin, but of superior grain and texture. The horse hide is rounded by the tanner, as seen in Fig. 18. The butt, A, is removed because of its substance making it unsuitable for uppers; nature has provided a layer of horn underneath the corium, which after tanning is principally employed for stiffening boots. The coarse piece, B, which was under the mane, is also removed; the remainder of the hide being curried for best work.

Goat Skins, from India and the Cape, are imported in a dry state. But millions also come into the market tanned and tawed, from the same countries. In 1873 England received as below from—

Cape of Good Hope,.....	846,225	goat skins.
British India, ...	155,426	" "
" "	5,368,605	tanned and tawed
Madras,.....	5,002.473	tanned.
Total.....	11,372,729	

The majority are prepared for imitation morocco, or tawed for chamois leather.

Sheep Skins are imported in immense numbers from South America, Australia, and many other localities. But with them, also, an increasing number are imported in a tanned state. In 1873 England received from—

Germany, sheep and lamb skins,.....	395,185
Italy, sheep and lamb skins,.....	296.678
Turkey, sheep and lamb skins, ...	556,906
Uruguay, sheep and lamb skins,.....	414,517
Argentine republic, sheep and lamb skins,	3,707,100
Cape of Good Hope, sheep and lamb skins,	1,392,321
Victoria, sheep skins,.....	534,612
New South Wales, tanned, ...	28,695
New Zealand, tanned,.....	136,089
British India, tanned, ...	2,801,312
Madras, tanned,.....	2,434,493
Total,.....	12,697,909

These are tanned for much the same purposes as goat skins. Sheep skins make a more spongy and porous leather, and are available for many cheap and inferior goods, such as linings, aprons, wash leather, and skivers.

Many fellmongers do largely in sheep skins, simply removing the wool by careful liming of the skin on the flesh side. The pelt is reserved for export, as the large skins of England are much sought after by American tanners. As many as 7,425,078 undressed sheep skins were exported in 1873 to the United States, where they are generally split for skivers.

Pig Skins.—South of the Tweed the skin is generally allowed to remain with the bacon; in Scotland a few are tanned, especially for saddle work, for which they are well adapted.

Seal Skins are rather limited in supply, being obtained from Falkland Islands, Cape of Good Hope,

Newfoundland, Norway, and Jan Mayen Island—the last-mentioned place being especially resorted to by these mammalia at the breeding season, where vessels from Peterhead and Dundee, also Norway and Sweden, congregate at the end of March. Much cruelty has been perpetrated on these defenceless animals, from the large numbers of mothers slain before the young were able to take care of themselves. When tanned, the leather is principally enamelled; and of late years quantities have been dressed with the fur for mantles and other feminine attire. The numbers imported for 1873 were as follows:—

Cape of Good Hope,	15,845
Newfoundland,	415,593
Norway,	90,259
Denmark,	5,064
	526,761

Seal skins imported in 1875:—

United States,	100,201
Whale fisheries,	87,293
British North America,	372,083
Patagonia,	8,647

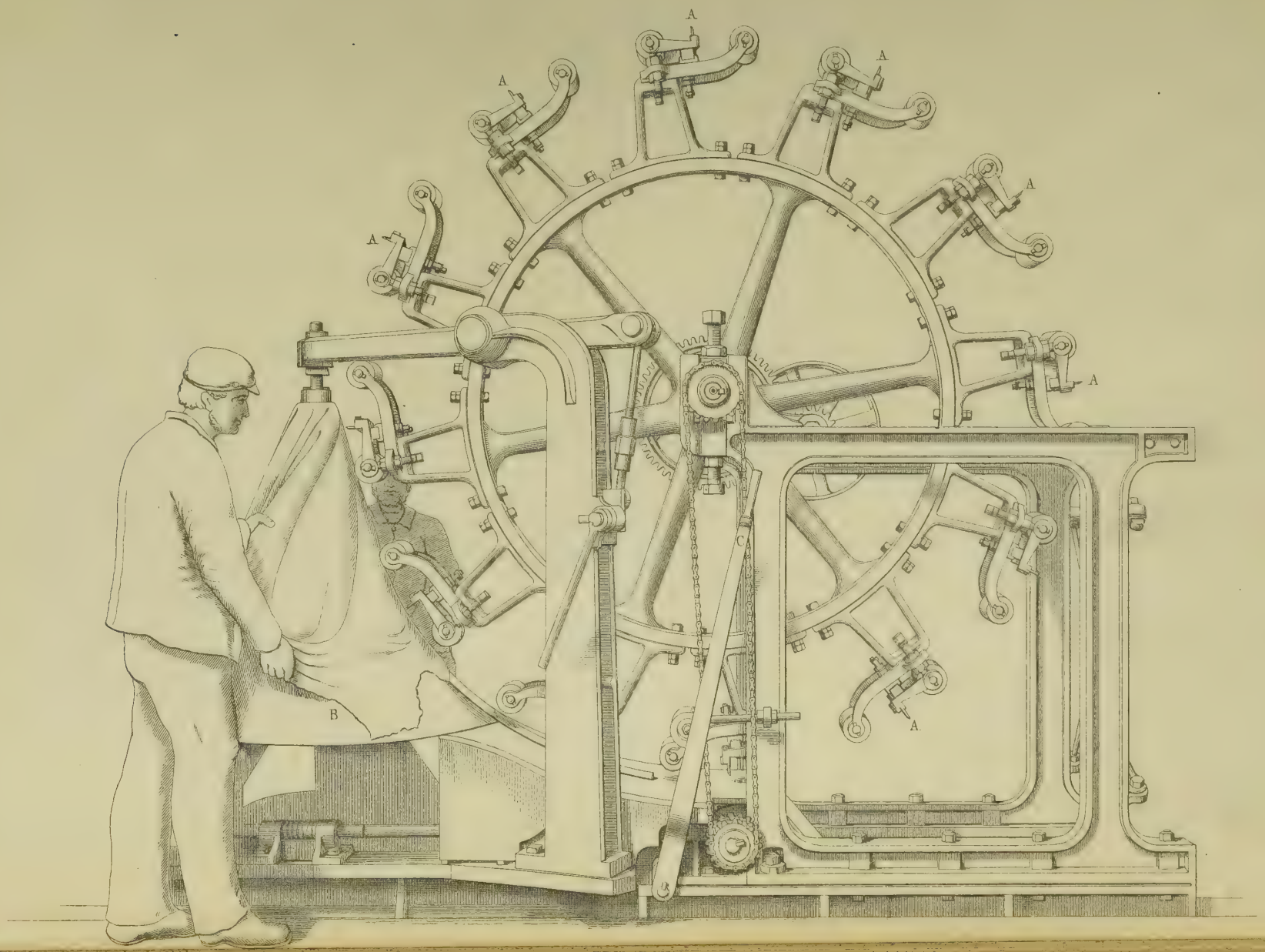
East India Kips.—The skins of a small breed of oxen peculiar to India. They are wrongly named kips, being from full-grown animals. Calcutta is the principal shipping port, the hides being brought to the bazaars by the native dealers from Dacca, Patna, Delhi, Cawnpore, and other districts. The majority of them are not stout enough for sole purposes, but make a cheap upper leather, which takes the place of English calf. They come to England as dry and dry-salted. The exports from India were as below:

1870,	13,675,997
1871,	16,300,150
1872,	20,043,959

Many of these hides are covered with plaster on the flesh side, adding considerably to the weight of the skin. The English tanners, after suffering largely from the fraud, refused to receive them in any such condition; so that in 1874–75 many tanners discontinued to tan them, and immense stocks of these plastered kips were stored in the London wharves and warehouses; and many a house connected with the East India trade has learned the great truth, that honesty is the best policy.

The Tanning of Hides.—*Preparatory Processes—Depilation and Raising.*—Hides, when brought to the tan-yard to undergo the tanning process, are presented to the tanner in two or three different conditions. First, as *market hides;* full of moisture, besmeared with blood and filth. Secondly, *salted;* from some foreign land, partially dry, with a considerable quantity of salt and dirt adhering. Thirdly, as *dry* hide; perfectly rigid, no moisture in the pelt, the whole cellular tissue of the hide with the corium thoroughly desiccated. Lastly, as *dry-salted;* if possible in a condition more intractable, and often loaded with dry earth or lime on the flesh. The tanner has to ask himself, how am I to treat these hides, so as to endeavour to bring them back to their original condition? This is not so easy a question to answer as may at first sight appear. With the hide fresh from the market, the usual process would be to wash the hide in clean water, and after draining for a short time, to pass it on into a stale or spent lime pit; but even here caution is required. Fresh hides, if exposed long to the action of clean soft water, especially to running water, are very liable to damage. Some descriptions of water are prone to reduce the pelt to a dangerous extent, not only washing out some albuminous properties of the pelt, but also exerting an injurious effect on the grain, technically known as *fretting the grain.* Such cases have been known to occur in three or four hours in summer weather. Some tanners pass the hide directly from the butcher's cart into an old stale lime pit, through which previously other hides have passed, so that nearly all the caustic properties of the lime have been destroyed. Such spent limes contain a considerable amount of free ammonia in solution, which is well adapted to soften and cleanse the pelt.

Wet-salted Hides.—The preliminary soaking in cold water is necessary, and attended with little risk, as the amount of salt will act as weak brine, preserving the condition of the pelt; but the water must be *cold.* These hides are allowed to remain in the water for three or four hours, then taken out from the pit to drain. As each hide is removed from the pit, care is taken to extend it to its full size, especially treading out any part which may have become partially dry in the folds. After lying in pile for one hour, they are again placed in the pit, to remain six or eight hours, according to the temperature, after which they are placed in a stale lime pit. *Dry* and *dry-salted hides* require considerable attention at this stage. Coming from tropical climes, the grain is often in a tender condition, or the hide may have become heated during the voyage. To soak them in cold water, especially soft water, would be almost certain to terminate in their destruction. To remedy this, the pit in which the hides are soaked must be supplied with brine, so as to raise the barcrometer 30 degrees or more, thus retarding to a great extent the too rapid action on the pelt; or carbolic acid may be added to the water, especially in warm weather. Borax may also be available for the same purpose, if of sufficient strength. Both of these will maintain the condition of the hide for a month or more, if necessary. The preliminary soaking cannot be hastened; the pelt must be thoroughly permeated with the soak before it is in a condition to absorb the lime or other depilatory. A hide or skin partially soaked would always retain a hard horny feeling, which no after treatment can remove. To expedite the process of soaking, it is usual, at a certain stage of the treatment, to break the hides on the flesh, over the beam or in the stocks, where the repeated beating of the hammers breaks the film of the flesh, and renders the pelt more porous. A few more days in the soak will be required to prepare them for the limes. During the winter the time allowed for the soaking of hides and skins may be lengthened with


A
A
A
A
A
A
A
B
C

advantage. A small quantity of sulphide of sodium is said to be used by some tanners to assist in the softening.

In our ordinary stocks all the power is applied in simply lifting the heavy hammers, which when released from contact with the tappet fall by their own weight, and thus stock the skins in the pan. Figs. 19 and 20 represent an improved double-headed stock or fulling mill, as made by Middleton of Leeds. The centre of each hammer is hollow, into which a square chamber is fixed; a shaft, A, passes through the centre of this chamber, and is attached by plumber blocks, B, to the sides of the pan. On the shaft are placed two eccentrics, C, C—one for each hammer. The revolution of the shaft brings these eccentrics into contact with the side of the

Fig. 19.

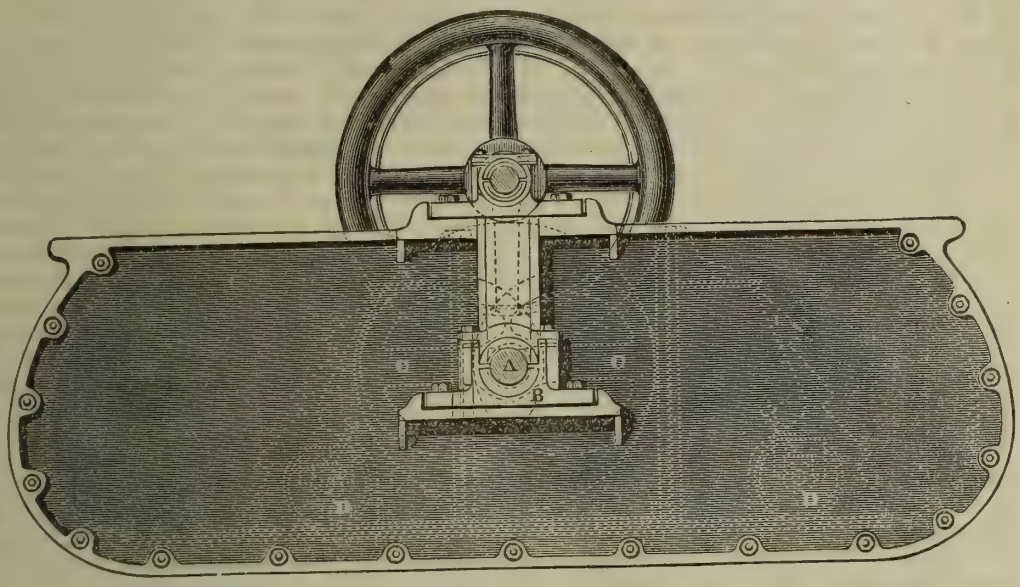
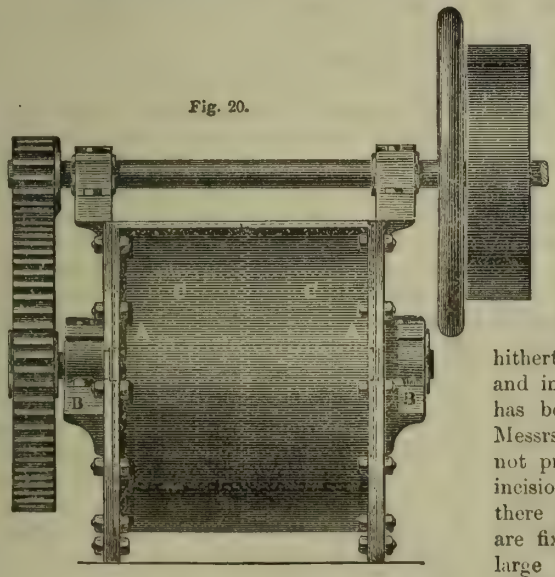


Fig. 20.



chamber, and the hammer is propelled in one direction; the same eccentric, on completing another half revolution, comes in contact with the opposite side of the chamber, and the hammer is propelled in the reverse direction. It must be noticed, that although both eccentrics are represented, in order to prevent confusion only one hammer is given. To prevent the hammers from dragging on the bottom of the pan, two large rollers, D, D, work at the base of the hammers. This machine works very smoothly, and with little noise. It is capable of stocking three times the quantity of any other stocks. Plate I. represents Messrs. Appleyard's, of Leeds, "patent fleshing machine." Many attempts have been made to construct a machine which would efficiently remove the flesh from the inner side of the skin; but hitherto all such attempts have proved failures, and in some instances the risk of damage thereby has been increased tenfold. The machine which Messrs. Appleyard have brought into notice does not profess to remove the flesh from the hide by incision with a sharp edge. The knives, of which there are a number (marked A on the engraving), are fixed at right angles to the periphery of the large wheel. The knives are placed between a pair of rollers, the one preceding, the other following it, so that the skin is kept in position, and prevented from buckling or getting into folds. The large wheel makes about forty revolutions per minute, so that the knives act by simple concussion: the blade is brought into contact with the hide, which in its rapid revolution knocks off the flesh.

The hide or skin is placed on a circular cone, B, the shape of which is constructed to exactly correspond with the sweep of the wheel, A; this cone, B, turns slowly with a horizontal movement, so that every portion of the hide is brought into contact with the knives as they revolve; the lever, C, is held by the workman, who is thus able accurately to adjust the distance between the knives and the cone on which the hide moves, so as to remove much or little flesh as he pleases. This machine will, it is believed, dispense with hand labour, and thereby considerably reduce the cost of production, and increase the freedom from cuts and galls.

Swelling and Depilation.—After soaking, the hides are removed into other pits to be treated with some depilatory, for the purpose of removing the hair; it is desirable also that the agent employed should at the same time raise or swell the substance of the hide, so that it may facilitate the entrance of the tannin in the after process.

Lime has for centuries been the principal depilatory employed both in England and on the Continent. The carbonate of lime—or chalk, from which it is obtained—being pretty universal, and therefore ready at hand, and its simplicity in action, may account for the favour with which it is looked upon by the trade. Much has been said and written against its use; yet it must not be forgotten that the best leather which the world produces is prepared for the tan with lime. The chemistry of the process would appear to be very simple. The caustic solution of lime coagulates the semi-fluid between the cuticle and the corium, thus loosening the roots of the hair, and freeing the epidermis from the true skin. It also unites with the fatty matter present in the cells of the true skin, forming with it a kind of soap; at the same time swelling the fibrous substance, and destroying a considerable portion of the albumen of the skin.

The mode of working is as follows. From four to six pits are worked in what is known as a *round;* two pits being the live or strong limes, four stale or partially spent limes. The hides fresh from the soak are first placed in a weak or stale lime through which other hides have previously passed, thus to a great extent destroying the caustic properties of the lime; in this pit they remain for about twelve hours, when they are hauled out of the pit, and allowed to drain on the side. The thick milk of lime at the bottom being stirred with a plunger, the hides are again thrown back into the same pit; here they remain for two or three days, being hauled out each day. After this time they are removed to a stronger lime, to undergo a similar process; at the end of a week or ten days (in the case of ox hides) the hides are sufficiently swollen to fit them for the lime pit, which is prepared in the following manner:—From 4 to 12 lbs. of lime per hide are placed in the empty pit; water sufficient to cover it is added; great heat is generated by the chemical action; the lime, combining with the water, becomes a hydrate of lime. Time being allowed for the cooling, more water is added, thus forming a milk of lime. The hides remain in this *lime* pit four days, by which time the substance of the hide should be sufficiently raised, and the hair readily removable. Having thus briefly sketched the usual course adopted in the depilation of hides with lime, it is but right to explain that great difference of opinion exists between tanners, as to the amount of lime to be employed, and the time during which the hide should be subjected to its action. Some are in favour of *low liming*, whilst many are equally believers in *high liming*. A tanner in one yard will employ 12 bushels of lime to unhair fifty foreign hides, another would only give 3 or 4 bushels. Presuming that the measures are the same in each district, and that a bushel of fresh lime will weigh about 56 lbs.; in the one case 672 lbs. would be used, whilst 224 lbs. would represent the other. Lime is but sparingly soluble in water—15 grains to the gallon. A lime pit holding 500 gallons would really hold in solution 7500 grains, or rather more than 1 lb. of lime. Of what use then are the 223 lbs. which yet remain undissolved and floating in the water with the hides? The chemist would insist on the fact, that only that which was soluble could exert any influence on the pelt. Such is theory. But it is evident that the pelt will absorb all the active soluble lime near, and will require a continued supply of the same. A considerable excess of lime must therefore be allowed to remain in the pit. The lime disintegrates and decomposes the gelatinous tissue of the hide, evolving ammonia; it also unites with the oil in the fat cells, forming a soap, and expands the substance of the hide. In old stale limes a considerable amount of free ammonia is present, which may be utilized in softening the skin, and preparing it for the active lime. The large quantity of lime used by some is, no doubt, wasteful in every sense of the word, as the lime whilst present in a caustic condition must be acting injuriously on the pelt, eating away the very nature of the same, as every ounce of gelatin destroyed implies the loss of nearly two ounces of leather. As has been noticed previously the coriin, or albumen of the hide, is dissolved by lime, therefore the less that can be employed the better. Experience has also proved that the ordinary method of making a fresh lime for every pack of hides is doubtful. Some tanners having once made a lime pit, after the first pack of hides has passed through it, add a smaller quantity of fresh lime to the same, and bring out another pack of hides. This is repeated three or four times; so that one pit having been started with 6 bushels of lime, has, by the addition of 2 bushels more after each pack, brought out as many as five or six packs. It is asserted that this may be continued until the pit becomes supercharged with ammonia and animal matter, thus neutralizing the effect of the lime, which, instead of raising, reduces the pelt. This may arise partly from the free caustic ammonia, partly because of the dissolved gelatin enabling the liquor to take up more lime, which is soluble in gelatin solution. Our forefathers are said to have kept ox hides in lime for twelve months; if this was the real state of the case, the solution must have

been very dilute, and some difficulty must have been experienced in maintaining the condition of the pelt.

Depilation by caustic soda has been employed. The ordinary carbonate of soda is rendered caustic by the addition of lime to a boiling solution; after agitation the insoluble carbonate of lime subsides, so that the clear supernatant solution of caustic soda is withdrawn, the proportions employed being 10 parts soda to 8 parts of lime. The solution very rapidly raises the pelt; but unless the hides are suspended in the solution, or continually handled in the pit, the edges of the hides are acted on, but the other portions remain to a great extent unaffected by the soda. The alkali unites with the fatty portions of the hide, thus more effectually cleansing the interior of the pelt, and preparing it better for tanning. It has been but little used in England. *Sugar* was patented by Dr. Turnbull, in 1844, as a depilatory. The saccharine solution is prepared with 14 lbs. of coarse sugar to 100 gallons of water. The skins are allowed to remain in this solution from eight to ten days, being handled daily. When the skins are sufficiently raised they are removed from the sugar, and, after draining, are immersed in a strong solution of sea salt, by which the cuticle contracts, and becomes easily detached from the skin; the pelt after washing in clean water is ready for the tan-house. This process appears to be scientifically correct; but thirty years have passed away since the patent was obtained, and no tanner appears to have adopted it. The reason why it is difficult to explain. It is not improbable that Dr. Turnbull's theory failed, like many others, from his deficient acquaintance with the practical details of the trade.

Calcium Bisulphide (CS_2), in a concentrated form, or as present in waste from alkali works, has been patented several times. A concentrated solution, or rather paste, of calcium bisulphide, applied to the hair side of a well-soaked hide, will in a few hours remove the hair freely; unless well applied it is liable to leave little patches of hair, which are afterwards difficult to remove. It exerts no injurious action on the pelt, one objection to its use being the unpleasant smell which it evolves. The sulphuret does not raise the pelt, so that the use of acids is necessary to prepare the pelt for the tanning. Alkali waste, or the gas lime from the gas-works, which is identical in composition, but of a milder nature, in the course of four to eight days effects the same purpose. If the statement can be substantiated it will be a boon to the trade, from the great saving of gelatine which is now lost in the liming process.

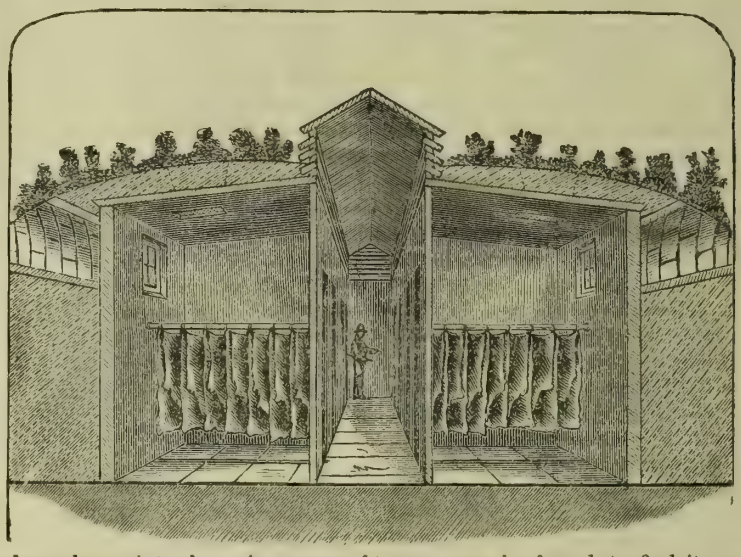
Sulphide of Sodium, in crystals of a dark brown colour, have recently been introduced to the notice of the trade. It appears to be looked upon favourably by German tanners, but in England has yet to overcome the proverbial prejudice against all innovations. Herr Eitner, of Vienna, has done his utmost to induce the trade to give it a fair and honest trial. He places the process before the public in the following extract from the paper issued by him: — "The method for using the sodium sulphide is very simple, and is performed as follows. The skins are laid out flat on the ground, with the hair uppermost, and are well brushed over on the grain side with a solution of sulphide of sodium. The best method for doing it is for one man, with a wooden bucket, to pour the liquor on the skin, commencing at the head and keeping well to the middle line; whilst another with a long-handled brush spreads it so that it reaches every portion of the surface, the head and back getting most, as the hairs are there longest, and closest, and most deeply set in. When every part of the grain side has been well rubbed over, the head, legs, and tail are folded in, and the hide rolled up. Thus rolled, the hides are piled in a warm place, or covered with a green hide to keep them from drying. In the space of fifteen to twenty hours the hair will be detached and ready for removal. The liquor for pouring on the skins in the manner just described is prepared in the following way:—A suitable weight of sulphide of sodium is dissolved in hot water. The commercial sulphide is in more or less dark-looking crystals, and varies considerably in quality, as we shall presently show. The sulphide dissolves quickly and readily if 5 pints of water are allowed to 2 lbs. of sulphide. The solution thus formed is very thin, and unless thickened would run off the hides. The best thickening is *milk of lime*. Chalk or pipe-clay may also be used: 3 parts of lime are allowed to 1 of sulphide, or rather more if the lime is poor. The lime is well stirred in the solution, so as to become intimately incorporated with it. The mixture must be neither too thick nor too thin. It should diffuse itself readily over the surface, lying amongst the hair, and not running off at the edges. A tanner in a large way of business has written to me on the subject as follows:—'You know that I tried the sulphide process as long ago as 1873, but without succeeding to my satisfaction. When the hides were brushed over on the hair side, and piled, the hair was speedily loosened, but not enough to come off well, and its removal proved difficult in proportion as the hides were left longer in the pile. The hides themselves were flexible enough, but rather dry to the touch. I then tried the following methods:—The hides were brushed over and piled until the hair was detached; they were then placed in a pit, and turned over several times every two hours. At the end of five or six hours they were unhaired with the greatest ease in a fulling stocks. I afterwards discovered that hides treated with sodium sulphide on the inside dry very quickly, which is the true reason why the hair does not come off well. To obviate this, it occurred to me to pack the hides, brushed over and folded as before, in a vat filled with water, pressing them down hard and leaving them there for twelve hours. The experiment succeeded perfectly. The hides rose gradually above the sides of the vat. The absorption of water had increased their volume; the hair came off readily. For the last two years I have treated all my small skins, and some of my large ones, in this way, without having occasion to regret

it With sole leather I have obtained equally good results, in respect both of the quality of the leather and the weight. I have ascertained that hides unhaired with sodium sulphide weigh heavier on the average by 10·4 per cent. than limed hides.'"

Charcoal.—ANDERSON of Inverkeithing obtained a patent for the use of finely-ground charcoal as a depilatory, in 1871. The skins after soaking are placed in a pit with enough water and charcoal to make a thin paste: the operation proceeds with more certainty if the temperature is maintained at 70° Fahr., when in four or five days the hides will readily unhair. During the process no perceptible odour of ammonia is recognized. The patentee gives it as his opinion that the chemical action is as follows:—The oxygen present in the pores of the charcoal acts chemically on the fatty matters, which are principally located near the roots of the hair in the glands. This fatty matter, containing carbon, will unite with the oxygen in the charcoal and the hydrogen of the water, thus forming carbonic anhydride and hydrocarbons; these are given off as gas. Thus in reality a kind of combustion takes place within the pores of the hide, destroying the gland, and thus loosening the hair without detriment to the hide. Other chemists, however, believe the process to be simply one of putrefaction, in which charcoal acts merely as a deodorizer.

Cold Sweating.—This is not an English process *as yet;* but as it is one of the most important American systems, it is desirable to give it a place here. A sketch of the sweat pits is given in Fig. 22, and explanatory remarks taken from J. S. SCHULTZ'S admirable papers:—"The sweat pits of the tanners should be constructed of stone or brick. These structures may be wholly above ground, and should be so placed that a wheelbarrow may be run from

Fig. 21.



the floor of the beam-house into the main passage of the sweat pit. These passage-ways should be wide, not less than 6 or 8 feet. The height of the main passage-way should extend above the surrounding pits, and by this *lantern* construction both light and air can be secured in the passage-ways below. The pits themselves should extend from both sides of this main passage, and be connected with folding-doors wide enough when open to admit a wheelbarrow. Each pit should be large enough to contain one pack of hides, and high enough to admit the hanging of a side doubled, with a space fully 2 feet above and 1 foot below the racks, from which the sides are suspended by tenter hooks. The width of the pits should be about 8 feet. This will give space for two tiers of sides, and a small passage for the attendant to pass to make his examinations. The temperature of these pits is held under control by steam and cold water, with which the main passage is amply supplied by means of pipes. A properly constructed pit should have a false bottom, under which the steam may be forced, to find its way in condensed spray up through the suspended sides. When too warm, cold water may be thrown from the mouth of a sprinkler over the whole surface, and will in a few minutes cool the whole space, and leave a desirable moist atmosphere. When in proper condition the pit will stand at a temperature of 60° to 70° Fahr., with globules of water standing on all parts of the suspended sides, occasionally dropping in thin condensation from the ends of the hair. Each pit should have at least four lights, 7 by 9 inches, in the end, with a lantern ventilator on the top, the latter to be controlled in its opening and closing by a cord. These pits should be covered on top by timbers, flattened on three sides; they should be heavy enough to hold up at least 2 feet of earth. This earth sodded over, and kept well watered, will amply protect the pits from the rays of the sun. The ammonia which arises from these pits will produce a most luxurious growth of grass, vines, or flowers on this earth covering. The sides of the

pits should be protected by a banking of earth or spent tan; the former is the most desirable. With pits thus constructed, and under proper control, hides may be properly sweated in from three to seven days, usually about four or five. The sides should be hung on the racks by tenter hooks, either suspended by the shoulder or from the pate and butt. As the sweating process advances with greater rapidity in the top than the bottom of the pit, and as the thicker portions of the hide resist the action of the sweat longer than the thinner portions, it is desirable, as far as practicable, to hang the pates and butts higher than the shoulders and bellies, or the position of the hides must be changed as the process advances."

After the hides are sweated they are either removed to the fulling stocks to be unhaired, or by some tanners treated with lime to plump them. This process is especially applicable to the tanning of dry hides; although Schultz asserts that he has known the green salted Texas hide produce 73 lbs. of leather to 100 lbs. of green hide. This is a large gain on the English system of liming, which only averages 60 to 65 lbs. to 100 of salted hide. It was asserted by many writers on the subject, that the cool sweating process was not one of decomposition, as no ammonia was evolved. This, however, is more than doubtful, as it is probable the ammonia would be carried off with the water. Schultz speaks of the ammonia as being valuable for vines and flowers.

Borax.—Very recently attention has been directed to the use of concentrated solutions of borax for unhairing hides. Borax is well known to possess the property of keeping animal tissue in a moist condition for months, without decomposition. It has yet to be proved in England.

The different materials thus briefly noted may be divided into three classes:—1st, lime and soda; 2nd, sulphides of calcium and sodium; 3rd, cool sweating, charcoal, sugar, and borax. Lime and caustic soda are strong alkalies, visibly swelling the pelt, and destroying much of the albuminous properties of the same. The sulphides, though strong in their action, yet, by the very rapidity of the depilation, remove the epidermis without injury to the true skin.

Cool sweating, charcoal, sugar, and borax may be regarded as a class in which no deleterious agent is brought to bear on the pelt; but in which moisture, kept in check by temperature and antiseptics, attains the same result. The general theory has been, that during the process a certain amount of decomposition must ensue, during which ammonia is evolved. This is borne out by the fact, that hides treated with lime, or caustic soda, evolve large quantities of ammonia; but this is doubtful when hides are treated with sulphides, as ammonia is not perceptible. With cool sweating, charcoal, and borax, ammonia does not appear to be one of the products; or the quantity is so small, that it is an open question with interested parties. May not lengthened soaking, especially under favourable circumstances, such as warmth, with the addition of other sulphides, originate a destruction of the hair bulbs, so that sulphuretted hydrogen is evolved without any detriment to the pelt? It is well known that dry skins, in a strong brine, will after a few weeks generate a large amount of *sulphuretted hydrogen*.

The subject of depilation is one of great moment to the tanner; and that such is felt to be the case is evident from the many new plans which are continually being broached in the trade journals. One great objection to the use of lime is not only the loss of gelatine during the depilation, but also the necessity to remove every trace of lime from the pelt, or the leather would be hard and brittle. With all light leathers this is especially required, as the presence of lime would be inimical to their flexibility and softness. To remove the lime *pure*, either dogs' or hens' dung, is the agent employed. These materials are steeped in cold water. The hides, after depilation and fleshing, are allowed to remain in the menstruum from one to three days, according to the temperature. The carbonate or chloride of ammonia present in the excrement undergoes decomposition; the chlorine uniting with the lime forming a soluble salt of lime, which is expelled by the tool of the workman from the pores of the skin. For the same purpose glucose, or grape sugar, is now employed in some localities, and appears to answer as well as the more objectionable *pure*. It is also safer in hot and thundery weather. Muriatic acid, with many of the weaker vegetable acids, such as acetic, lactic, and oxalic acids, may with advantage be employed; but hitherto the expense has prevented their general adoption.

Before the hide or butt passes from the limes into the tan house, it is taken by the workman, who places it across a semicircular frame, called a beam, Fig. 23; with a two-handled knife, Figs. 24 and 25, he removes the hair, after which another workman operates on the other side of the hide, cutting off all the flesh and fatty matter which has been left by the butcher. After washing in an adjoining pit the hide is rounded, as previously explained;

Fig. 22.

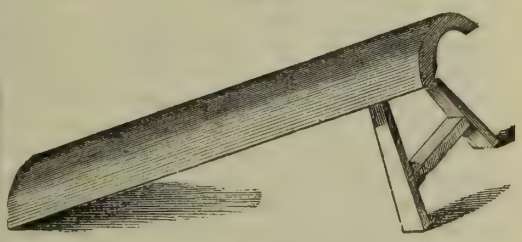


Fig. 23.



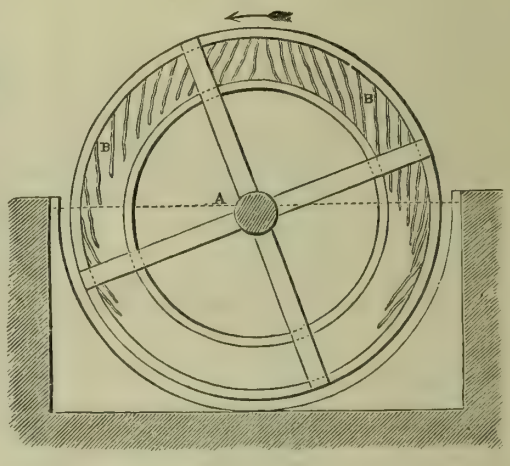
Fig. 24.



the butt, bellies, and shoulder are sent into the tan house, while the cheeks and odd pieces are dried for the glue merchant.

The Tanning.—The usual process adopted with green goods fresh from the lime yard is as follows:—A certain number of pits are reserved for the reception of these goods. They are termed suspenders, and are filled with a weak mild liquor. It will enable us better to master the subject if a glance is given at the condition of the butt. The butt is in a condition to undergo the tanning process. As it leaves the lime-yard it is full of moisture, swollen to twice its original substance; all the cellular tissue is distended, and what may remain of coriin or albuminous properties very fluid, and easy to be expelled by pressure through the pores. The pelt is in such a condition, that the careless application of warm water, or too violent agitation in a weak menstruum, may not only waste the coriin, but also let down the pelt, so that it would be difficult afterwards to repair the damage. Experience also has shown that the colour of the future leather in great measure depends on the treatment at this stage of the pelt, which may be compared to a sponge, in a condition to receive and absorb any tannin with which it may be supplied. It was not unusual in some tanneries to pass the butts from the lime-yard, for a short time, through some pits containing a strong solution of tannin; the object being to case-harden the grain and the flesh, just enough to prevent any loss of pelt, and maintain the substance of the butt. This process effectually sealed the pores, inclosing, it is true, the loose and fluid coriin, but as effectually preventing the exit of the lime. So the butt afterwards had to be let down in condition to remedy the mischief done at this stage. The aim of the tanner should be to maintain the substance of the butt, retaining all that goes to make leather; yet to keep the pores open, so that the lime may readily combine with the acetic and gallic acids present in the weak liquors, and thus be expelled from the skin. Within a very recent period the usual process was to place the butts loosely in a horizontal position, in a weak and stale solution of tannin. They were removed from the pit twice a day, being allowed to drain for a few minutes. The effect of this treatment was soon visible, when the butts were thrown up twelve hours after to drain. The butts had a tortoise-shell appearance, in spots shaded from light amber to dark brown. The butt as thrown into the pit carried down with it a certain amount of air, which was retained in the folds as the pressure increased. So the lime, as it exuded from the pores, met with the tannic and gallic acids, and in the presence of the confined air turned the grain to a dark colour. It is true that by careful handling afterwards some of this can be rectified, but not all. The present method, which is generally adopted, certainly appears to be preferable. It is as follows:—A certain number of pits called washers, 6 feet in depth, 7 feet in length, and 4 feet 6 inches wide, are filled with the partially spent liquor which has become sour, holding a small percentage of tannic acid, with a considerable quantity of acetic and gallic acids. The butts are suspended by cords in the shoulders from poles placed across the pits, so that they hang freely, without touching each other; the liquor thus has free access to every surface of the butt, and its action is equal all over the pit. The lime present in the pelt unites with the acetic and gallic acids, thus becoming soluble, and freely exuding through the pores. Butts treated in this manner, and carefully watched, will increase in substance, and gradually all the lime will be expelled, leaving the butt in a condition to proceed to the second stage—namely, the handlers. Seeing such to be the case, many drew the inference that their leather had simply in its earlier stages to be brought into contact with fresh supplies of this sour liquor, and the process of tanning would proceed very rapidly: forgetting that this part of the process is preparatory, being one of cleansing and swelling. Quite a volume could be written, giving accounts of the different mechanical

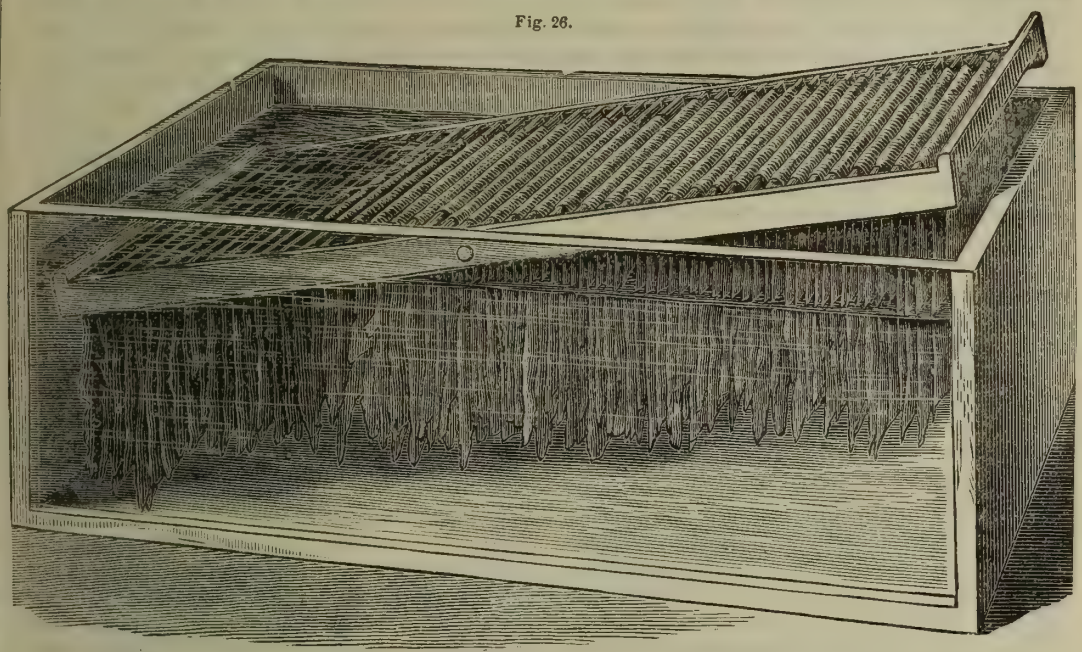
Fig. 25.



contrivances which have been constructed to expedite the tanning process at this stage. Just a few may be selected to illustrate the subject. Mr. Bede, of Colyton, Devon, about forty years since, having plenty of water power, constructed a circular frame 10 feet in diameter, by 5 feet in width (Fig. 26); a strong wooden shaft, A, carried across the pit formed the centre of the drum; arms radiating from the shaft at the periphery carried a stout wooden ring, in which were inserted a number of wooden rods with two hooks, on which the butts, B, B, were suspended by one side internally. The butts, fresh from the lime-yard, were hung on the brass hooks until the machine was about half full. The wheel or drum was allowed to revolve slowly, one-half of the drum being above the liquor, the other immersed. Thus every butt was alternately half its time out of the liquor and exposed to the action of the air; the effect of this became speedily apparent, the colour of the butts rapidly darkening until they became almost black. Two faults existed in this plan, the atmosphere darkening the colour, and the violent agitation of the butts

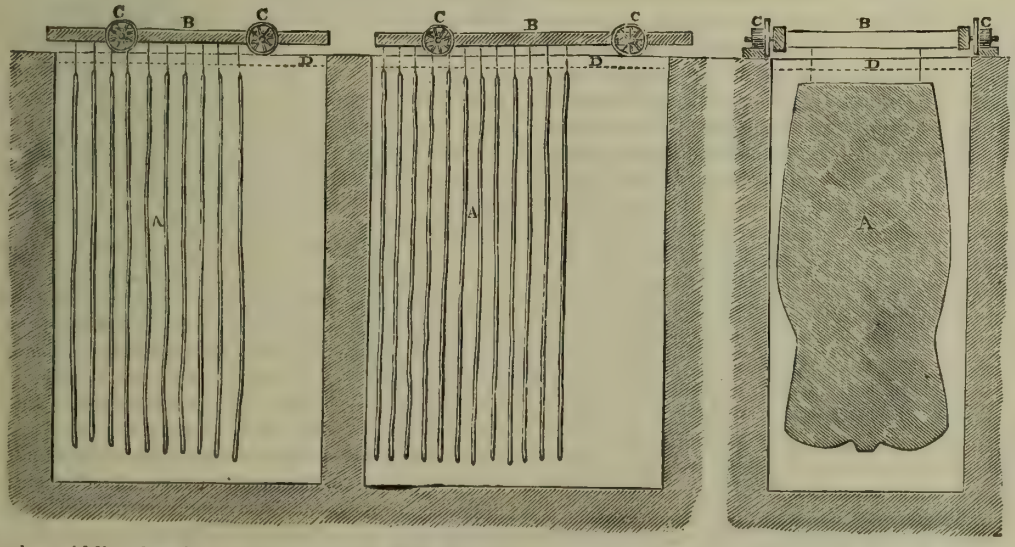
causing considerable loss of gelatine. Mr. Stephen Cox, of Bristol, attempted to improve on this machine, by immersing nearly the whole of the wheel in the liquor, so that the action of the air was reduced to a minimum. But the loss of gelatine from the revolution of the wheel still remained. Both have been abandoned. A compromise between the revolving and stationary suspenders has had its advocates. The frame on which the rods rested was constructed so as to be free of the sides of the pit; and being

Fig. 26.



supported by a strong shaft in the middle, it was readily worked on the see-saw plan, one side depressed as the opposite was elevated. The Americans seem rather in favour of this rocking machine (see Fig. 27). It is apparent, however, that when in motion the butts are exposed much too freely and unequally to the air, as those at the ends of the two arms have more contact with the air than those

Fig. 27.



at the middle; by this motion also the filth which collects at the bottom of the suspenders is very liable to be stirred up, which imparts a bad colour to the leather. Another machine, the invention of Mr. W. N. Evans, of Bristol, the object of which was to present fresh supplies of sour tanning liquors to the butts while suspended, with but little agitation, is shown in Fig. 28. The pits were made 6 feet 6 inches deep, 7 feet in length, and 5 feet wide; three pits were worked in a row. On the edges of the pits

were fastened pieces of wood to form a tramway, D; on this tramway was placed a frame, B, just the size of the pit, borne on brass wheels, C. Fifty butts, A, two on a pole, were placed in each pit; these occupied 5 feet of the frame, thus allowing 2 feet play. The frames were slowly propelled backward and forward by means of a mangle movement attached to the steam engine; five or six times a minute being the speed at which the tram travelled. The pits being of large size contained a considerable amount of acids, which by this plan were brought into contact with the fresh pelt, so that the lime rapidly exuded, and the butts increased in substance. The filth of the butts, collected at the bottom, was not disturbed by the slow movement of the tram. The colour and grain thus produced was excellent. The inventor does not regard the machine so much as a tanning, as a good purgative and grain-setting machine. This plan is available only for sour liquors; if employed with the harsher woozes from the taps, a bad colour is the result, and flesh and grain are liable to become case-hardened.

Another plan, which has but few followers, is yet worthy of more attention. The butts, as removed from the water, are suspended in the usual manner, but are not moved in the pit for twenty-four hours, if the liquor is mild and sour; the result is a beautiful grain. The lime, as it exudes from the skin, comes in contact with the gallic and acetic acids, forming a sort of scum on the surface; this appears to protect the grain at this stage, and the process, though slow, is satisfactory. At the end of the twenty-four hours the butts are removed into another pit, when the scum is washed off; they are allowed to remain another twenty-four hours, and the process continues.

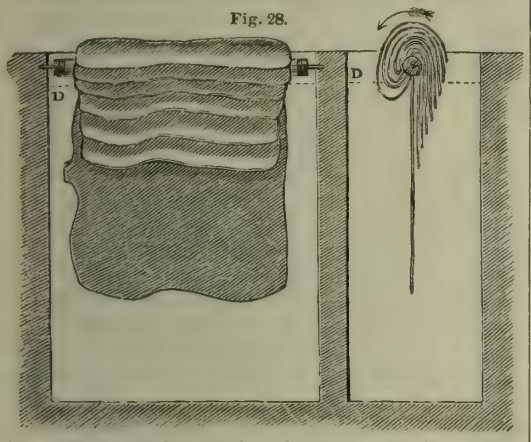
At this stage it must be borne in mind that the skin is in that impressible condition that slight modifications of the process may effect startling changes in the pelt. Whilst it will be apparent to most that liquors of too sharp a character may at this stage be prejudicial to the pelt, it is also certain that mild sour liquors must have such an amount of acids, such as tannic and acetate, to keep up the condition of the pelt, since if by any mistake the balance is on the other side, the lime which remains in the pelt more than neutralizes the acids. In other words, if two packs are passed through a pit which contained only acid enough for one pack, especially if the butts are agitated with any violence, the result may be disastrous; as the gelatine will exude from the pelt, and float in large quantities in the liquor. It is therefore very false economy to endeavour to extract every vestige of tannic acid from the suspenders. Each tanner must use his own judgment as to the weakness of the liquor in which he suspends his green goods. No rule can be given in this matter. When oak bark is the principal tanning material employed, liquor standing at 3° to 4° barcrometer may be considered as spent, and thrown away; but with mixed materials, such as valonia, myrabolans, and divi, which generally impart a turbidness, 10° to 13° barc. will often not be too high to be thrown away. One or two experiments with Ramspacker's tan-tester will enable the tanner to ascertain the amount of tannic acid in these weak solutions. One precaution is necessary, that the liquor to be tested be filtered until it be *quite clear*. This is often a matter of difficulty, from the presence of lime and organic matter. Nor must the tanner be misled by some of the chemical tests, which are now and then advanced as ready methods of ascertaining the weakness of a liquor. For instance, a drop or two of ferric sulphate applied to a spent liquor may yield a considerable apparent precipitate, which would yet be too weak to keep up the condition of the pelt. Nor must the tanner forget, that a treatment which may be suitable and right in a district where hard water is used, would probably be suicidal in another locality, where soft water abounded. It is known with some degree of certainty that the butt, after leaving the suspenders, is capable of imbibing any reasonable amount of tannic acid that may be presented to it, provided the pores of the skin can be kept open. For this reason, many plans have been adopted to force the tan into the pelt. Some keep their butts suspended all through the process, which enables them to move every butt daily; but the drawback to this system appears to be the loss of bloom, which is considered so essential to good leather, and the large number of pits required. Messrs. Cox and Drake obtained patents for expediting the process of tanning. The butts being sewn at the edges, so as to form bags, were filled with liquor, which was by hydrostatic pressure forced through the pores of the butt, the bag being maintained in its upright position by a frame. The penetration of the tanning was imperfect; the skins were bulged by the unequal pressure, and the fibrous structure of the pelt strained and distorted. This plan has been recently revised, but with no good result. Acting on the theory that the pelt was something like a sponge, others passed the butts from one pit to the other under rollers, which, removing all the spent liquor, introduced the pelt into another pit where was a fresh supply of good liquor, which would rapidly combine with the gelatine in the butt. Such was the theory, but the end attained was a *thin* spongy leather.

In 1863 H. Hamer of London took out a patent for improvements in tanning, and apparatus employed therein. The patentee says—"I suspend the hides or skins within an air-tight vessel, so that the tanning liquor which the vessel contains may come in contact with every part of each hide or skin; I exhaust the air from the tank; and further, I keep the tanning liquor in motion during the process, so that it may sweep off from the hides the film of spent liquor immediately it is formed. The hides are hung on laths at the upper part of the frame, transversely of the length of the tank; as the hides are moved by rack work, the liquor presses first on one side, then on the other. The tank is connected with an air pump, and is exhausted during the process. Air may also be forced in to a pressure of 5 or 6 lbs. to the square inch." The leather produced

by this method is good in colour, but appears lacking in weight and substance.

Tremlett & Wilson of Exeter have in operation another plan, a sketch of which is given in Fig. 29. About twenty butts are affixed by one side to a large shaft which works over the middle of the pit; as it slowly revolves the butts are folded over or around the shaft, and in the revolution each butt as it turns over frees itself from the shaft and hangs suspended its full width in the pit; each butt thus obtains a fresh contact with the liquor in the pit on every revolution of the shaft. The shaft revolves just on a level with the liquor in the pit, D. It will be well to notice at this stage a patent process taken out by Evans in 1873. All practical men have experienced considerable difficulty in the treatment of green goods, on their first introduction to the tanning woozes. The pelt is liable, if the process is carried on too rapidly, to become case-hardened. The grain side especially becomes tanned, inclosing the lime, and prevent-

Fig. 28.



ing to a great degree the after process of tanning. When the grain is thus sealed, the future leather when dry will look dark in colour, very brittle, liable to crack, and will *buff* indifferently. The flesh side is not affected to the same extent. This explains the reason why, in the first stages of tanning, the process is so protracted. Care has to be taken to prevent this *case-hardening*. The object of the patent mentioned above is to provide a remedy for this by shielding the grain by some composition before, or at an early stage of, the tanning, so that the pelt can be pushed on into much stronger woozes than it otherwise could bear, and the process be shortened thereby. The butts are removed from the rounding table, freed from lime as far as possible, allowed to drain on horse for twelve hours, then rubbed dry, and grease or thick dubbing carefully rubbed over the grain, and the butt removed to be suspended in strong liquors. The following figures will show the rapidity with which the fresh pelt absorbs the tannin; the woozes being tested by barcrometer when placed in the pit, and each morning after. On the fourth day the stale liquor was withdrawn and fresh supplied :—

	First Day.	Second Day.	Third Day.
First liquor.....	65½ ..	49½ ..	46½ .. 44
Second liquor,....	74¼ ..	66½ ..	59½ .. 50

The mode in which the patent is now applied is to allow the butts to be suspended in the usual manner for two or three days, when they will have become coloured, and the lime near the surface exuded. They are then placed on horse to drain as before. The grease is well rubbed in to the grain, and the butts may then be placed in very strong woozes with satisfactory results, the weight and solidity of the leather thus treated being much in advance of ordinary tannages, and in one quarter of the time.

It is right to mention here, that there are a few tanners who, regarding only the time, and ignoring all other considerations, place their green goods very rapidly in strong woozes, and by mere strength of liquor force it through the skin. But the leather resulting from such treatment is bad in colour and texture, and a few years since would have been unsaleable. This method is referred to only to be deprecated, and as worthy of the dark ages.

The Handlers.—These are a series of pits to which the butts are removed after leaving the suspenders. As previously remarked, some ignore suspension, and pass their butts at once from the beam house into the handlers, but this is rather the exception. The handlers are composed of from four to twelve or more pits, which work in what is technically known as a *round*. A round of six pits would comprise two *dusters*, containing the oldest packs in the round, which are not only treated with the fresh liquor, but also with a certain quantity of finely-ground oak bark placed between each butt, and four *floaters*, which, as the dusters are moved into a fresh pit, follow in regular order, the oldest pack taking the place vacated by the duster, the last floater being the pack which has most recently been received from the suspenders. Twice or three times in the week, according to the length of the round, one of the *dusters* is thrown up to drain, preparatory to receiving a fresh liquor; the floaters following are shifted from one pit to the other. The removal of the last leaves a pit without any butts, partially full of the sour, stale liquor through which all the butts in the round have previously passed. This sour liquor is generally pumped back to the suspenders, where all the tanning properties remaining are absorbed by the green goods, and then thrown away. Returning to the round, the pit is cleaned out, and a fresh, bright liquor from the brewing vats is pumped into the pit, the strength of wooze varying from 20° to 35° by barcrometer. The butts from the duster, which have now drained for two or three hours, are thrown in one by one, and loose ground bark scattered over each butt; the object of the latter being to prevent too close a contact, so that the liquor may be able to penetrate, and also by its tanning properties to sustain and feed the pelt. Exclusive of the shifting, in most yards the floaters are taken up to drain once or twice a day, and then returned to the same pit. This is termed *handling*. Having described the present mode, it will be interesting to contrast the original plans adopted by our forefathers. An empty pit being provided, a layer of ground bark, 2 inches in depth, was placed evenly over the bottom of the

pit; on that was laid a hide, then another layer of bark, 1 inch in thickness, and again another hide; thus alternately bark and hide were laid until the pit was full, a larger quantity of bark covering the whole, which was termed the *hat*. To this was added the right quantity of fresh water, the hides were allowed to remain for six or eight weeks, then the hides were removed from the pit, and the partially spent bark and tan pumped off. The same process was carried out the second time, the hides remaining a week or two longer. As the hides approached the end of the process, the time was considerably lengthened between each renewal. The leather manufactured by this primitive process was excellent—tough, mellow, and of good colour; but the time occupied was from two to three years. This process may still be seen in France and other countries on the Continent. It was a great advance to prepare the woozes in separate pits. The bark, valonia, or myrabolans being thus presented to the pelt in a concentrated form, materially shortened the process of tanning. The brewing pits are known in the trade as *taps* or latches. Returning to the handlers; the butts generally remain in them from one month to two months, by which time they should appear to be struck through one-third of the substance of the pelt. In most cases the old packs will have acquired a peach-like bloom, the substance of the pelt having considerably increased and much consolidated. The butts are now moved into the *bloomers* or *layers*, in which pits they remain until finally tanned.

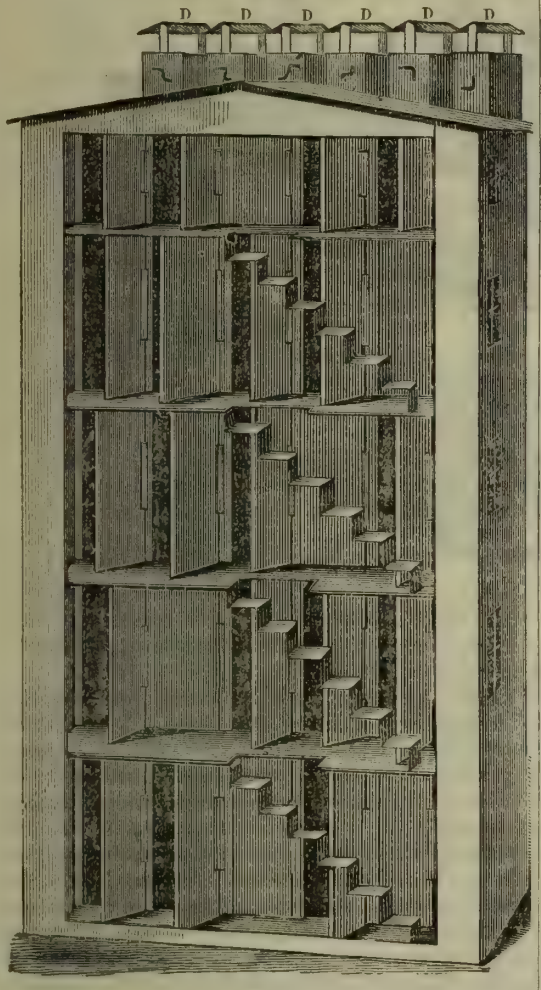
Before passing to the layers, it will be appropriate here to pass under review the waste liquor, which, pumped from the handlers into the suspenders, is usually thrown away. It is a matter of considerable doubt with many how far such spent woozes should be permitted to run into the sewer, or be returned to the taps in the place of clean water. Clean water no doubt is safer, as the sour wooze returning to the taps will carry with it a certain amount of acetic and gallic acids, with lime and organic matter. These woozes, if continually returned to the taps, gradually change the whole character of the liquors, until a great proportion of their tanning properties are destroyed. The liquor becomes very sour, thick, and syrupy, in some cases approaching the consistency of thin treacle. Such liquors are termed *ropy;* and when arrived at such a stage that the tanner can see the liquor adhering to his walking stick, it will need his best attention to prevent the utter ruin of all his liquors, which in these days are often valued at thousands of pounds. The remedy for this is to stop the cause—let no more sour woozes be returned to the latches, but let them be ruthlessly thrown away. Replenish the taps as quickly as possible with a large quantity of new material, and continue this until all the strong woozes in the yard have been returned to the taps, and thus revived. It must not be supposed that there are no conditions under which these sour liquors may be beneficial. A limited return of the spent woozes may be of benefit to the suspenders occasionally, to give the amount of acidity which is required.

The different conditions connected with the locality, the water, and especially the principal tanning agent employed, must be well weighed by the tanner. If the leather be bright and full with clear water only, it would be unwise to economize by saving the spent liquors. After this digression, we return to the layers or bloomers, of which little need be said. The butts on leaving the handlers are transferred to pits, termed *layers*. Here they are laid down in stronger liquors, with a larger amount of bark. The first layer, the pack would be placed in liquor of 40°, and remain down without moving for ten days; the second layer, the pack would receive an increase of 3° or 4° of strength, and remain about a fortnight, thus gradually increasing in strength of liquor and in the duration of the time. At the end of five or six months the thinner butts would be tanned, and fit for the drying loft. Most tanners would give their stouter butts one or two extra liquors, in which case they would remain down four or five weeks, and in liquor 60° or more. As every tanner has his own notions as to the strength of liquor and the material of which that liquor shall be made, it is only possible to speak in general terms of the treatment of butts in the layers. Some use liquors which are made entirely from valonia, using bark only for *dusting*—that is, to be placed between the butts; others employ two-thirds of valonia and one-third myrabolans for their liquor, and in some cases one-half of valonia and one-fourth each of mimosa and myrabolans, the penetration and colour of the mimosa counteracting the softening properties of the myrabolans. Of divi divi, as has previously been stated, its use is exceptional; and when employed it is kept distinct from the other liquors, and only used when the staple materials have risen in value. As the butts increase in age, the amount of *bloom* or ellagic acid (?) deposited increases also; and when tanned, which is ascertained by an incision in the stouter part of the butt, the sectional cut will reveal the fibrous texture of the skin of one colour throughout, if carefully tanned. The presence of lime in the earlier stages is visible by the skin when cut showing a much darker tinge, spreading inward from both grain and flesh side. It is a matter of doubt how far the system at present adopted in *layers* is correct; as, for instance, the butts placed in a layer with bark between each, and liquor standing at 50°. At the end of three or four days the liquor will only record 45°, and at the end of ten days 40° will be the limit; and whilst the thin edges of the butts have had more contact with the liquor than they required, the stouter portions of the skin have been in the centre of the pit, and under considerable pressure. The tannin also between each butt will be rapidly extracted without any means of replenishing until the time has expired (say three weeks), when the pack is taken up and a fresh liquor given.

Numerous objections present themselves as to the continuance of the present system. From the moment the butts are laid away the liquor commences to deteriorate, whereas it should rather improve

in condition; and it is equally certain that the creation of ellagic acid implies corresponding loss of tannic acid, resulting from lengthened exposure to the sun and air. Hitherto the great difficulty against the adoption of a more rational system has been the prejudice in favour of bloomed leather: tanners were making goods according to order. But now that the introduction of the American leather has been so universal, it is possible that this standard of quality will in some measure be modified, and a longer

Fig. 29.



period of suspension, with more frequent changes in the layers, will be the probable result.

The Drying.—The leather after draining in the tan house is carried to the drying shed, where, hung on poles, it is exposed more or less to the wind. During the summer, care has to be taken that the desiccation is not too rapid, especially during the prevalence of easterly winds, as butts in some tannages become quite black on the edges when exposed to the full force of the east wind, and are liable to crack even when partially dry. A treatise on the "Leather Manufacture" has appeared from the able pen of J. S. Schultz of New York, a work which has been carefully compiled, and is full of information on the most approved methods of tanning in vogue in the United States. Advantage has been taken of Schultz's kind permission to give sketches of some of the labour-saving machinery which are employed in American tanneries.

The "turret dryer," Fig. 30, will speedily be constructed by all who have occasion to erect new drying lofts. Our present plan of *luffer boards* is open to many serious objections, among which may be enumerated the following:—The little control the shedman has over the currents of air that pass through the loft; the leather suspended near to the luffer boards becomes overdried and bad in colour; that hanging in the centre of the loft remains damp, and in continued bad weather becomes mildewed. But in the "turret dryer" advantage is taken of the knowledge that rarefied air *ascends*; and if proper exits, D, for the heated air are provided at the top of the building, the quantity and temperature can be regulated with the greatest nicety. The goods being dried in the dark will certainly give a better colour. Two other considerations should be mentioned in favour of this method of drying:—First, the saving of time and labour which is now required in moving the leather in our present system; secondly, the economy in erection, as one roof may cover the whole series, and the cost of making and fitting luffer boards is saved, which is a considerable item in the expense in erecting our present loft.

The process of desiccation is often aided by the additional heat generated from hot water or steam, carried around the lofts in iron pipes. This plan also guards the wet leather from damage in frosty weather. Some hides or butts, for sole or strap work, are occasionally dried *rough*, without any other preparation. But the majority have to undergo two operations, namely, those of *striking* and *rolling*. The leather is taken down from the poles when a little more than half dry; the butts are placed together in small piles, covered with cloths, in which position a little heat is gradually imparted to the pile. The experienced workman arrests that process when he considers they are in good *temper*, or in other words, in a mellow working condition. The butt is thrown across a large wooden tressel, termed a horse, with the grain side uppermost; the workman, with an iron instrument with three cutting edges, Fig. 31, proceeds to lay the grain

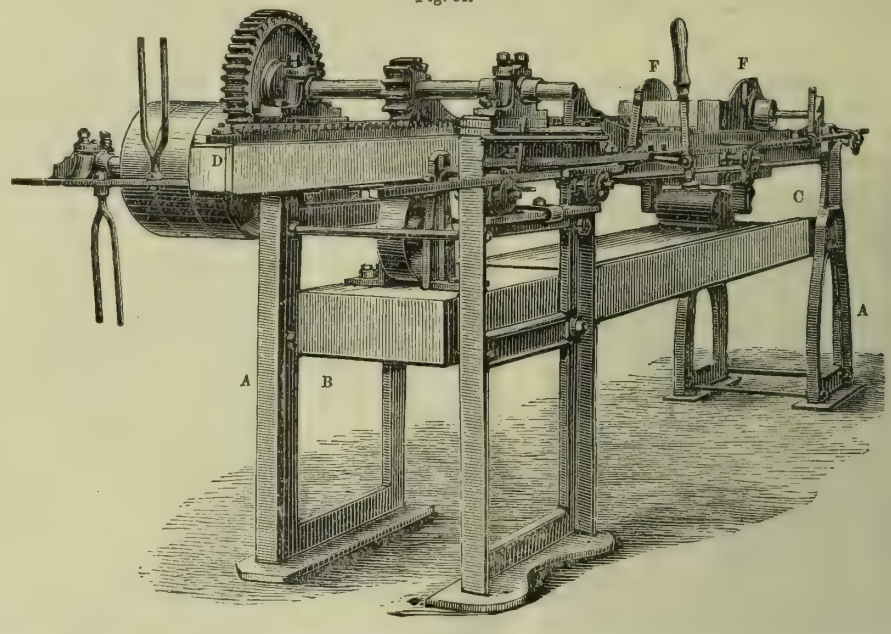
Fig. 30.



down, during which process a large amount of the ellagic acid or bloom is forced out of the skin, and the surface of the butt is rendered more level and smooth than originally. The butt being allowed to get a little dryer, is then passed under a heavy brass roller, which gives a face and polish to the grain, and consolidates the leather; which is carried from the rolling bed or machine to frames or racks to dry, and

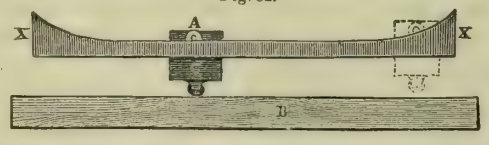
when fully dry is ready for the market. The ordinary method of rolling leather was simple but laborious: a smooth surface of wood about 8 feet square, technically known as the *bed*, was laid on the floor of the loft; a square iron box weighing from 10 cwts. to 30 cwts, furnished on the under side with a brass roller, rested upon the bed: to the box was attached a strong handle of wood, by which means the workman was able to drag the roller in all directions over the bed. This was laborious work, and in some cases required two men to work the machine. Of late years several makers have introduced rollers driven by steam, among which mention may be made of Newall and Barker's rolling machine, also Harding and Melbourne's. But the steam rolling machine which is shown in Fig. 32 is the invention of

Fig. 31.



Mr. Keetch of Bristol, and is now in satisfactory work in several large tanneries. B represents a stout plank 8 inches in thickness, which is supported on iron frames, A. A roller, C, traverses this bed, being propelled backwards and forwards by a stout pole, D, which has on its upper surface an iron rack, which corresponds to small pinion, *f*. It will be noticed that two flanged brass rollers, F, are fastened to the side of the iron box; these small rollers run on the iron rails, which are parallel to the course of the

Fig. 32.



roller. The use of these small rollers is explained by Fig. 33.

The roller in position, A, is resting its full weight on the leather as laid on the bed, B. But as the roller, C, arrives at the end of the course at the position, D, the small rollers now take the weight of the whole, and being forced up the incline, X, raise the brass roller from contact with the bed, B. This enables the workman to remove the butt, or shift it in any position he pleases. At the opposite end of the course is another incline, up which the rollers pass; thus every time the roller traverses the length of the bed, two opportunities are given to the workman to shift the leather on the bed. In other rollers the treadle is used for the same purpose, but this is remarkable for its simplicity in action.

Some remarks will be appropriate here as to the testing of the quality of dry leather. The exterior of the grain should be of a light fawn colour, a sectional cut showing several shades darker. Looking at the fresh cut, the thickness of the grain should be barely perceptible; if otherwise, and the grain is evidently swollen, it is probable that the skin was exposed too long to the action of lime in the earlier stages. The cut edge of the leather may be inspected with a magnifying glass, not vertically, but at an angle of 15°. If the leather is well tanned, the spaces between the fibres will stand out prominently and of a brilliant lustre. Leather undertanned shows hollow between the fibres, and the colour dead. The *impermeability* of leather was the general test of the old-fashioned shoemaker, who, placing the sole in the basin of water, would note the length of time taken in soaking. Partially tanned leather, acting like a sponge, readily imbibes water. This has been one of the tests of the Philadelphia Exhibition, as also the weight and substance per square foot, and the amount of the wear and tear by friction.

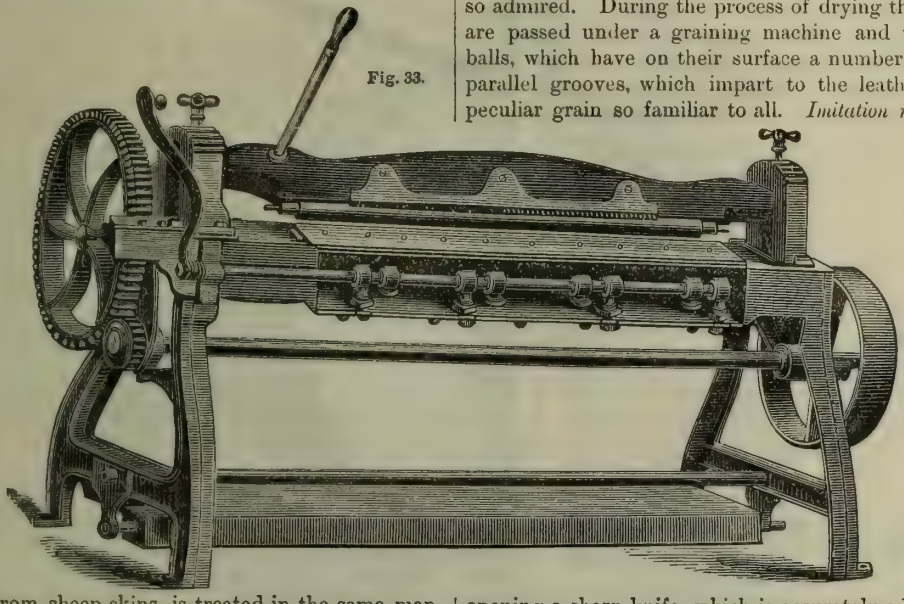
Good oak bark tanned leather *buffs* brightly; a very minute slice taken from the surface of the grain should show a cut several shades brighter than the

exterior. Eitner asserts that when a piece of well-tanned leather is placed in a test-tube and exposed to strong acetic acid, no change is visible on the surface of the cut; the texture remains unaltered. But imperfectly tanned leather, in acetic acid, first grows dark; the gelatinous tissue swells and becomes transformed into a glutinous and transparent mass, whilst at the edges two dark non-transparent stripes are recognized, the skin here being fully tanned.

Fancy Leathers.—Among these may be reckoned real and imitation morocco, roan, skiver, and Russian leather. As more attention has been given in this paper to the leading branch of the trade, namely, the heavy or sole leather, it will necessitate that remarks on the fancy leathers should be considerably curtailed. Fancy leather is mainly manufactured from the skins of sheep, goats, kid, and seal.

Morocco Leather.—The true morocco is made from goat skins. The depilation of the skin is very similar to that of heavy leather, lime being the agent, which is neutralized by *pure*, or pigeon's dung. After fleshing and unhairing, the skins are repeatedly rinsed in water. The two edges of the skin are sewn together, thus forming a bag, with an aperture at the neck. The bag is nearly filled with a strong decoction of sumach; the workman, blowing into the bag, distends it to its full extent. The mouth being tied, the bags are floated in a tank containing a weak solution of sumach, where they are repeatedly stirred with plungers. The distension by wind insures a good grain, and the strong sumach inside finds ready access to the pelt through the flesh side, and the principle of endosmosis and exosmosis is practically illustrated on a small scale. A few hours are sufficient to tan skins in this mode. The skins are opened, rinsed, and removed to the dye-house, where decoctions of cochineal, logwood, acetate of iron, and sulphate of indigo produce the brilliant colours so admired. During the process of drying the skins are passed under a graining machine and wooden balls, which have on their surface a number of fine parallel grooves, which impart to the leather that peculiar grain so familiar to all. *Imitation morocco*, made from sheep skins, is treated in the same manner, the only divergence from the usual course being, that before the tanning commences the skins are subjected to great pressure in a hydraulic press, to expel as much as possible of the oleaginous matter they hold in the pores. They are tanned in sumach, being thrown loosely into the pit; the dyeing and after processes being very similar to the treatment of true morocco.

Fig. 33.



Roan is prepared from sheep skins, and undergoes the same manipulation as imitation morocco, with the exception that the graining is dispensed with, leaving a smooth surface.

Skiver is comparatively a modern innovation, the wet sheep skins being passed through a splitting machine (Fig. 34), which makes a clean and level cut between the grain and the flesh, dividing the skin into two distinct layers, one containing the grain, the other the flesh side. In the openings between the two portions of the machine, at the level of letter A, the skin is introduced, and as it is drawn through the opening a sharp knife, which is accurately adjusted, and working at considerable speed, divides the skin into two distinct portions, or in other words, splits it into two thin layers. These thin divisions tan very rapidly in sumach, the flesh side of the skin selling as wash leather for common purposes; the side having the grain is reserved for bookbinding, hat linings, &c.

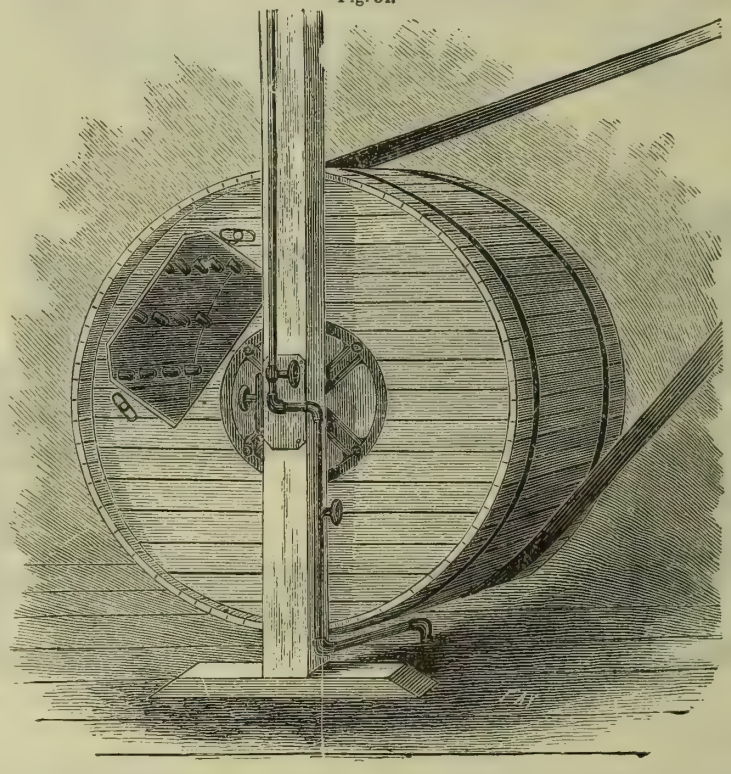
Russian Leather comes under the list of fancy leathers, and is well known for the peculiar smell of birch-bark oil which pervades it. This kind is known in Russia as *youft*, the number of skins tanned being considerable, as is gathered from the interesting sketch of M. Kittary of leather in Russia. The skins tanned in different governments are given below—

	Skins of Youft or Soft Morocco Leather.
Viatka,	280,000
Tver,	250,000
Kazan,	200,000
Moscow,	150,000
Koursk,	150,000
Orenbourg,	100,000
	1,130,000

The depilation of the skins is effected with lime combined with ashes, called *shadric*. After unhairing they are repeatedly washed and kneaded to free them from lime and potash, then placed in vats containing gelatinous matter; meal mixed with warm water is added; in this mixture they remain from six to seven hours, being constantly handled during that time. The acetic acid which is generated rapidly removes all traces of the lime; they are then removed to the tan-house, and tanned in the ordinary way. After the tanning the leather is dressed in the following manner:—The skin is smeared with a mixture of birch tar and melted fat, the proportion to each hide being ½ lb. of tar and 1 lb. of fat. The leather is then dried.

Chamois Leather.—This manufacture cannot strictly be termed chemical, as the pores of the skin are simply impregnated with oil, without any chemical combination. Goat, sheep, and deer skins are used, besides the split sections of many other thin hides. The liming and puring of these are similar to morocco. But when the hair and flesh are removed the grain side is subjected to a process called *frizing*, in which the grain is removed by rubbing with pumice stone. This treatment is only necessary when whole skins are operated on, much of what is termed chamois being simply the inner half of a sheep skin which has passed through the splitting machine; such will not need to be *frized*. The skins are now transferred to the fulling mills or stocks, having been

Fig. 34.



previously smeared with oil—fish oils being generally employed; the action of the hammers forces the oil into the pores of the skin, until they become thoroughly saturated. The excess of oil is removed by an application of a warm potash lye, after which they are hung up to dry.

Tawed or White Leather.—The skins of kids and sheep are used for this purpose. The kid has been reserved principally for glove work; the skins employed being taken from very young animals, require careful attention in the liming. From the lime pit they are placed in vats containing a mixture of bran and water, the proportions being 40 lbs. of bran to 20 gallons of water, the acetous fermentation removing the lime, and likewise filling and raising the pelt. When the skin is ready it is rapidly passed through the alum bath, which is composed of 12 to 18 lbs. of alum in 12 gallons of water, to which is added 2½ lbs. of salt; in cold weather a little more salt would be required. The skins are passed through this bath rapidly, not being allowed to remain in the liquor more than a few minutes. The finer descriptions of skins, especially those intended for gloves, are operated on in a sort of churn, an addition being made to the alum bath of 15 lbs. of wheat flour, and the yolks of fifty eggs. The skins being placed in the barrel, it is caused to revolve rapidly; the emulsion tends to soften the skins and prevent any tendency to brittleness. Fig. 35 represents the common form of the stuffing wheel, which is now in constant use in most tanneries, being a very useful machine for a variety of purposes. It is cylindrical, made of wood stouter than ordinary hogshead; the interior is studded with a number of

wood pegs, which in the revolutions of the wheel catch the skins in the fall, and tend to macerate and soften the pelt; these machines are also used for mere washing purposes at different stages in the tanning process. The chemistry of the process is, according to Berzelius, by the reaction of common salt (chloride of sodium), and alum (sulphate of alumina and potash), there are produced chloride of aluminium, sulphate of soda, and sulphate of potash. The chloride of aluminium becomes resolved by the skins into a subchloride and a perchloride; the former, which is the least soluble, combines with the animal tissue, while the latter, with the sulphates of soda and potash, remain in solution in the liquid. The skins, after leaving the bath, are partially dried, when the workman draws them with considerable force over a semicircular iron fixed on the top of a stake, the effect of which is to impart great softness and pliability to the skin.

Currying has to do more directly with the thinner hides and skins, which are designed for the uppers of boots, for coach and harness work; the stouter hides, both foreign and English, are reserved for sole purposes and strap work. Many of the stoutest hides are, however, curried to a certain extent for heavy harness work and for belting. With light goods, such as shaved hides, kips, and calf skins, the currier has to manipulate them, so as to render them impervious to moisture, flexible, and with a certain amount of colour and polish. It will not be within the province of this paper to give in detail all the various operations of the currier, but rather a general summary of the usual routine.

The skins or hides as received from the tanner are full of bloom, the grain often drawn and creased, the flesh side under the best of circumstances very rough and uneven. The aim of the tanner has been to remove all superfluous flesh, but not penetrate or lay bare the pelt beneath the *areolar tissue* or film; but during the process of tanning the film is distended or broken, so that some amount of rough flesh has to be dealt with. There is also a hardness and rigidity about the leather which must be altered before it will be sufficiently supple for boot work. The first step is the soaking. The skins are placed in water for a short time, then thrown out one at a time on the beam, and skived—that is, rougher portions of the skin are removed, and the skin strained out. The workman then takes the skin and bait-shaves it—either the stouter portions of the butt and neck, or the whole surface of the flesh side. This removes the film, and penetrates some depth into the substance of the pelt. This is an operation requiring both skill and judgment on the part of the workman, who places the skin over a beam nearly vertical (Fig. 36), using a double-edged knife of a peculiar construction (Fig. 37), in order to insure a thin and even layer being removed; the edge of the knife is turned nearly at right angles to the blade, and held with power by the cross handle. The skin having been reduced to the desired thickness, is again placed on the table, water applied, and the surface of the grain slicked with a steel instrument worked at an angle of 45° over the grain, removing the draws and equalizing the surface; in some cases to the slicking is added a brushing with a hard brush of both the grain and flesh sides. This operation is repeated, some applying a little warm water to the skins, so as effectually to discharge from the skin nearly all the bloom held in the pores, which if allowed to remain would have imparted a brown colour, and prevented the grease and oil from incorporating with the pelt. This is one of the many anomalies of the trade. The currier has a preference for leather in the market which is full of this bloom, as giving thereby a certain amount of guarantee that the leather has been tanned with the orthodox material. The bloom is of no use to him, his first intent being to remove every trace of it. Thus because of prejudice he compels the tanner to waste

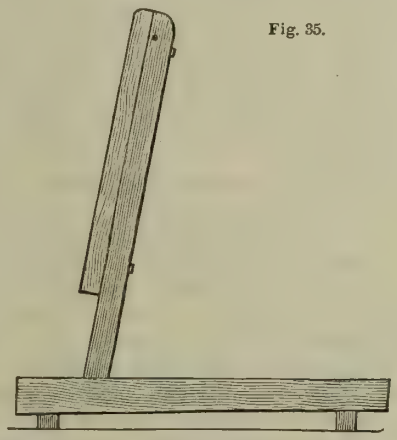
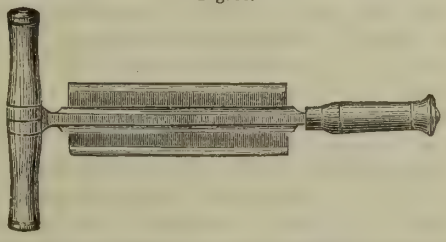


Fig. 35.

Fig. 36.



a certain proportion of his liquors to make this bloom; he himself purchases goods which weigh heavier from this very bloom, that he at the first stage removes. Tanners who are also curriers never trouble about bloom, the leather not having to pass through the market. The skins are tanned as rapidly as possible, without any deposit of bloom, and taken wet from the tan pit to the currier's loft. This adhesion to prejudice becomes more indefensible when it is patent to all in the trade that a great proportion of the bloomed leather in the market has been doctored to imitate oak bark; so that bloom after all is no guarantee. The bloom having thus been removed and the texture of the skin opened, it is now in a condition to receive the compo or sumach, which will more intimately unite with the fibre, giving colour, flexibility, and also enabling the grease afterwards more easily to enter and com-

bine with the pelt—from 15 to 20 lbs. being the complement for 5 dozen skins. Cold water is by some used with sumach; but when the rapid action of this material is considered, warm water should have the preference, as tending still further to open the pores of the skin. The skins are laid in the pit or vat carefully, and allowed to remain for a short time, are then handled, and again immersed; care being taken that the liquor has free access to every part. The skins in cold sumach are allowed to soak for two or three days, but with warm liquor twenty-four hours are sufficient. The skins are drained, then placed on a table to be sleeked, and while still wet the oil or dubbing is laid on with a brush. Some prefer oiling the flesh side first, afterwards the grain; others adopt the reverse. When all the grease has been laid on which is considered necessary, the skin is hung up to dry. The French curriers appear to stuff or grease their calf skins before samming them; or, in other words, stuff them while dry, placing them afterwards in warm sumach, which, they contend, softens them much more than our method—drawing the grease to the very centre.

In hides intended for harness work, which require a certain amount of rigidity, the sumach process is dispensed with; after soaking, the hide is roughly shaved, so as to level the flesh, then stuffed with as much grease as it will carry. The after processes connected with currying are of little interest to the general reader. The thinner portions of skins and kips are reserved for black grain or russet.

The information embodied in this paper is given as the result of thirty years' practical work in the trade; also friendly contributions from S. J. SCHULTZ of New York, H. R. PROCTOR of North Shields, and other tanners; from "Morfit on Tanning," BRANDE, and WATTS' "Chemical Dictionary."

LIME.—See CEMENT.

MAGNESIUM.—*Magnium, Talcium.* Symbol, Mg. Atomic weight, 24.

This metal was discovered by DAVY in 1808. He obtained it by electrolysis, using mercury as the negative pole, when an amalgam of the metal resulted; and also by reducing magnesia by passing the vapour of potassium over it at a red heat. In 1830 BUSSY decomposed magnesium chloride by potassium at a red heat in a porcelain crucible, and obtained the metal in large quantity.

BUNSEN found that the anhydrous chloride in a fused state was decomposed with facility by the voltaic current. A porcelain crucible is divided vertically for half its height by a diaphragm (a thin porcelain crucible cover answers), and closed in by a tile cover, through which two plugs of fire-clay traversed by charcoal stems enter the two halves of the crucible. These stems form the poles; that which corresponds to the negative pole is hollowed with cavities or channels for the purpose of retaining the magnesium, which, if this precaution were omitted, would float on the bath of fused chloride and be burned. Ten zinc-carbon cells are required.

A. MATTHIESSEN improved upon BUNSEN'S process by substituting for the anhydrous chloride, which is difficult to prepare, a mixture of the chloride of potassium and magnesium in nearly equal proportions, viz., three equivalents of potassium chloride to four of magnesium chloride. The solution of the magnesium chloride can be evaporated almost to dryness, and analyzed to find approximately the quantity of anhydrous salt present. After having mixed the two salts in the proper proportions with some ammonium chloride, the mixture is fused and electrolyzed by BUNSEN'S method. The cavities in the negative carbon point are not required, as the metal is specifically heavier than the fused mixture. A very simple and convenient way of reducing the metal, especially for the lecture table, is in a common clay pipe over a BUNSEN burner; the negative pole being an iron wire thrust through the pipe stem, and the positive a piece of gas-coke just touching the surface of the fused chlorides.

Although commonly classed amongst the metals of the alkaline earths, magnesium in so many of its properties resembles zinc, that it may more properly be considered as forming one of a group with zinc and cadmium. These metals are volatile, burn in the air when sufficiently heated, decompose water at high temperatures, are oxidised by dilute acids (hydrogen being set free), and form only one oxide and one chloride.

Magnesium is a silvery white metal; its fracture is sometimes slightly crystalline, sometimes fibrous. It is neither malleable nor ductile, but can be squeezed through a narrow orifice into ribbon or wire. It is fusible at a dull red heat, about 500° C. According to DEVILLE and CARON it volatilizes at nearly the same temperature as zinc, about 1100° C. Its specific gravity is 1·7430 (BUNSEN), 1·75 (DEVILLE and CARON). When heated to redness in air or in oxygen it takes fire, and burns with an intense light, forming its only oxide, magnesia. The light given by burning magnesium is very rich in actinic rays; it therefore renders valuable aid to the photographer in working at night or in dark places. According to a statement of TROOST, a magnesium wire of 97 millims. in length and 0·33 millim. in thickness gives by its combustion as much light as 64 candles, and this intensity is increased to 110 when the combustion takes place in oxygen. An equally intense and more economical light is obtained if, instead of pure magnesium, an alloy of magnesium and zinc is burned.

Dry air produces no action upon magnesium, but in damp it is tarnished, and covered with a coating of magnesia. Cold water is only very gradually decomposed by this metal. At temperatures above 70° C. magnesium decomposes pure water. THOMAS WOODS states that the quantity of heat developed by the combustion or oxidation of an equivalent of magnesium is twice as much as that produced by the oxidation of an equivalent of zinc. DITTE thinks this estimation too high, and places the calorific equivalent as, zinc 1, magnesium 1·61.

When brought into contact with hydrochloric acid

it ignites for a moment. Concentrated sulphuric acid dissolves it with difficulty. A mixture of fuming nitric acid and sulphuric acid does not act on it at ordinary temperatures. Heated in chlorine gas or bromine vapour, it burns into the chloride and bromide respectively. Heated in sulphur vapour or iodine vapour, it burns with greater brilliancy.

T. L. Phipson, who has brought to light many of the properties of magnesium, points out that, nevertheless, iodine and sulphur may be distilled over magnesium without altering it. He has also shown that silicic acid is not reduced by potassium or sodium, because these metals are highly volatile, and fly off before the crucible has attained the proper temperature; but magnesium, being much less volatile, takes oxygen from silica before it reaches its volatilizing point. Heated for some time in a porcelain crucible with excess of anhydrous silica, magnesium burns visibly if the air has access, and a certain quantity of amorphous silicon is immediately formed. If the silicic acid be in excess, a magnesium silicate is formed at the same time; if the metal is in excess, much magnesium silicide is produced.

Magnesium liberates carbon when heated with dry carbonate of soda at a temperature below a red heat, with formation of magnesia.

Nearly all the metals are precipitated from their neutral solutions by magnesium; when they are taken in the form of proto-salts, even manganese, iron, and zinc are thrown down as black powders. Aluminium, uranium, and chromium are only precipitated as oxides. Roussin suggests that it should be used as a precipitant of poisonous metals in toxicological investigations.

Magnesium forms many alloys. In making them it is necessary to avoid contact with air, and the fluxes must contain no oxygen. To prevent reduction of silicium from free and combined silica, and the loss of magnesium by volatilization, the fused mass must not be too long heated. James Parkinson prepares magnesium alloys of easily fusible metals—such as tin, bismuth, cadmium, lead, zinc, and antimony—by fusion in an atmosphere of hydrogen in a hard glass tube over the coal gas flame of a good air burner. The less fusible metals are alloyed in a flux, or in brasqued crucibles. Silver, gold, and copper may be fused and alloyed either in a flux composed of equal parts of fluor spar and cryolite, or of fluor spar and common salt; and, with the exception of zinc and cadmium, the easily fusible metals may be alloyed in like manner.

The flux should be fused in a stout Cornish crucible before the metal is added, and the magnesium secured to an iron rod by clean iron wire, so that it may be kept beneath the surface of the flux. A rod about a quarter of an inch thick and 3 feet long, bent at the end into the shape of an O of about 1 inch in diameter, is suitable. The magnesium should be secured with as small a piece of iron wire as possible. The metal must be fused before the magnesium is inserted.

The temperature of the fused mass is much lowered when the magnesium is first plunged into it, so that the flux thickens and adheres to the rod; but in a short time the temperature rises, and it again becomes liquid. The iron rod can then be removed. There is always a loss of magnesium by volatilization if the heat be continued after the metals are alloyed. The alloy should therefore be removed as soon as possible, and quickly cooled, either by pouring out into an ingot mould, or by cooling the crucible in water, taking care not to let any water come in contact with the alloy, or it would be much corroded.

The magnesium may be oxidised out of most of its alloys, by simply fusing it with sodium carbonate and carbon.

The colour of the metals alloyed with magnesium is not much changed; but their physical properties are remarkably changed, since, without exception, magnesium renders all alloys brittle; even "triple alloys" of magnesium with gold and silver, or copper and nickel, are remarkably brittle. Lead containing only 4 per cent. of magnesium is very hard and brittle. Platinum forms a very easily fusible alloy. Combination begins at a red heat with vivid combustion. For this reason magnesium cannot be prepared in platinum vessels. The alloy with zinc curiously enough tarnishes least of any alloy of magnesium.

The application of magnesium as a source of light has already attained much technical importance. Photographers use it for making enlargements, copying engravings, &c. Bunsen and Roscoe go even further than Troost in their description of the amount of light evolved by burning magnesium. They say a wire of the thickness of 0·297 millim. gives as much light as 74 stearine candles, of which five go to a pound. If this light lasted one minute, 0·987 mètre of wire, weighing 0·1204 grain, would be burnt. In order to produce a light equal to 74 candles burning for ten hours (whereby 20 lbs. of stearine would be consumed), 72·2 grains of magnesium would suffice.

Magnesium is very largely diffused through the mineral kingdom. It occurs as hydrate (brucite), carbonate (magnesite), with water (hydro-magnesite), chloride (carnallite), borate (boracite and hydro-boracite), phosphate (wagnerite), silicate (chondrodite), sulphate (Epsomite, or Epsom salt), and nitrate, also as silicate in a large number of minerals combined with other silicates, for instance, meerschaum, steatite, hornblende, asbestos, chrysolite, talc, soapstone, and many others. In the animal and vegetable kingdoms it is found chiefly as carbonate and phosphate.

Deville and Caron employ magnesium chloride for the preparation of the metal. They obtain this salt by evaporating to dryness a solution of magnesium chloride mixed with ammonium chloride, heating the residue till it melts, and pouring out the melted salt. The sal-ammoniac prevents the decomposition of the magnesium salt by the water of crystallization. The dry residue is then transferred to a red-hot crucible, so as to complete the operation quickly.

Magnesium chloride is volatile, like zinc chloride, and is capable of being distilled from porcelain vessels in an atmosphere of hydrogen. It is then obtained as a colourless, pasty mass, which solidifies with lamellar crystalline structure.

There is great difficulty in separating the last portions of ammonium chloride from the magnesium salt, and to this circumstance is attributed the frequent presence of nitrogen in magnesium prepared from this compound.

The flux employed is calcium fluoride. Pure crystals of this salt are powdered and moistened with concentrated sulphuric acid, and after some days washed with water. By this means the silica and phosphoric acid are removed.

A mixture is then made of—

	Parts by Weight.
Magnesium chloride,	600
Calcium fluoride,	480
Sodium,	230

This is introduced into an earthen crucible heated to redness, and the cover is kept down by a weight while the reaction takes place. When the action has ceased, a clear liquid remains, without any metal being precipitated. This is, however, disseminated through the entire mass as microscopic globules.

After stirring the melted mass, the crucible is taken from the fire; and after being left to cool for a few minutes, small successive portions of dry powdered calcium fluoride are added, so as to hasten the cooling, the whole being meanwhile stirred with an iron rod until it becomes pasty. By proper management, almost all the magnesium may be gathered together in a mass upon the rod before the denser saline substances become solid. If the metal should in the meanwhile take fire, the combustion may be stopped by throwing on it a little more calcium fluoride.

The magnesium is then separated from its slag by a few blows with a hammer. It should amount to three-fourths of the quantity equivalent to the sodium used. By melting the slag this proportion may be greatly increased.

Good results are also obtained by using a mixture of magnesium chloride with one-sixth of its weight of sodium chloride, or of the mixture of sodium and potassium chlorides (recommended by WÖHLER), and one-sixth of calcium fluoride. This mixture is melted with sodium, as above described.

Ingots of magnesium are cast by melting the metal with a mixture of magnesium and sodium chlorides with calcium fluoride. On gradually increasing the proportion of the latter salt in the melted slag, it is rendered less fusible than magnesium, and solidifies; at this moment the metal is poured off into suitable moulds. Or, the globules of magnesium, cleaned by means of nitric acid, are melted with mixed alkaline chlorides; at the moment of solidification the globules of magnesium become denser than the slag, and sinking to the bottom of the crucible unite into a button.

Thus obtained, magnesium contains carbon, silicon, and magnesium nitride. Magnesium is volatile at nearly the same temperature as zinc, and like it boils. DEVILLE and CARON availed themselves of this property in devising a process for purifying the metal. This they did by distilling it in carbon-lined vessels in an atmosphere of hydrogen.

The melting point of magnesium thus prepared is nearly the same as that of zinc. In the crude state the metal is very brittle, but when pure is pliable. It tarnishes in the air, but not more quickly than zinc, and the oxidation is never very considerable.

E. SONSTADT in 1863 patented a process for manufacturing magnesium, which is substantially the same as that of DEVILLE and CARON; the main difference being that he employs an iron crucible in place of an earthen one. He uses a mixture of sodium chloride and magnesium chloride; this he places with the necessary quantity of sodium in an iron crucible or vessel closed with an iron cover, and heats it to full redness.

To make his mixture he first prepares pure magnesia or carbonate of magnesia by decomposing magnesium sulphate with soda or sodium carbonate, washing the precipitate, drying it, and again washing, repeating this until the sulphuric acid is entirely removed. The pure magnesia, or magnesium carbonate, is then dissolved in hydrochloric acid, and sodium chloride added in such quantity, that for every part by weight of acid (1·152 specific gravity) there may be about 0·55 parts of sodium chloride. The residue obtained by evaporating the solution to dryness is fused in a platinum crucible, and poured out on an iron plate; this constitutes his working mixture.

In order to obtain magnesium from this mixture it is placed, with one-fifth of its weight of sodium, in an iron crucible with a close-fitting cover, and heated to redness.

If the proportion of sodium is much increased, the excess burns explosively when the cold fused mass is washed with water; if much less is used, the yield of magnesium is diminished.

The best results are obtained when the mixture of magnesium and sodium chlorides is roughly powdered before being treated with sodium. There should be a layer of the mixed salts at the bottom of the crucible, then the greater part of the sodium in large pieces; lastly, the crucible should be filled up with the rest of the chlorides interspersed with small pieces of sodium.

The crucible must be perfectly free from rust, and the cover should have an inside flange so as to fit closely, but need not be fastened down. The whole mass should be heated quickly up to, but not beyond, full redness. If the heat be raised too high, magnesium vapour forces its way into the air and burns brilliantly. It is not necessary for the heat to be continued for more than about half an hour after the whole crucible has become red hot. The iron is not attacked if air be excluded.

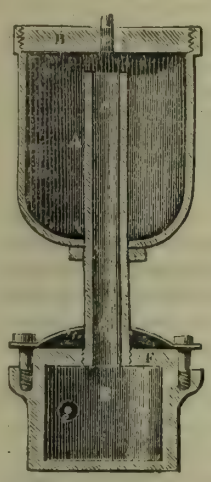
The magnesium thus obtained is purified by fusion in anhydrous chloride of magnesium, without any other flux. When the magnesium is pulverulent, it is thrown into a small quantity of magnesium

chloride already fused in a crucible. The crucible cover must be instantly put on, and the heat continued for a few minutes more or less, according to the quantity to be operated on. The cover is then quickly removed, and the mass compressed by a rather large and perfectly dry and clean iron rod. As the magnesium chloride begins to solidify (the heat meanwhile being diminished) the metal is compressed into globules, which then run together. When cold the lump of magnesium is washed first with dilute acetic or nitric acid, and afterwards thoroughly with water.

SONSTADT afterwards patented an ingenious apparatus by which DEVILLE and CARON'S method of purifying magnesium by distillation can be profitably carried out on a commercial scale.

Fig. 1 is a section of this magnesium still. It consists of two wrought-iron vessels, A and E, connected together by a pipe, *c*. These vessels can both be rendered air tight, and during the process of distillation they are so closed. The upper of the vessels is placed in a furnace and surrounded by fuel; in this the magnesium to be purified is placed. The under vessel, E, is fitted into a recess formed for it in the fire grating, or bars of the furnace, and projects below. The crude magnesium having been placed in A, the lid, also of wrought iron, B, is screwed on, and the whole apparatus being made air tight, a current of dry hydrogen is passed through the two vessels through the holes, *e e*, left for that purpose. When the whole of the air has been swept out, these apertures are closed by driving in steel plugs; but there is a small orifice left in the plug of the lower vessel, so that, when the apparatus is heated and the gas expands, the excess may be able to escape. This passage can be closed by a wire which is made to fit it closely.

Fig. 1.



The apparatus being charged, the fire is lighted around it, and the hydrogen, as it escapes from the small wire hole, *e*, is ignited and allowed to burn as long as it will, after which the hole is closed. The lower vessel, E, is kept cool by mopping it externally with water. The vessel, A, containing the magnesium should be heated to a bright red, approaching a white heat, and maintained at this temperature until the operation is complete.

The apparatus is then withdrawn from the fire and cooled; it is then taken apart, when the magnesium will be found in a more or less solid mass in the lower vessel.

In Fig. 1, A is the wrought-iron crucible; B, its cover, screwed on; *c c*, tube connecting the crucible and condenser, and screwed into both; D, lock nut to fix the tube, *c*, air tight; E, iron condenser with one-fourth inch hole, *e*, stopped with iron plug; F, cap to the condenser, held by screw bolts and clips.

MAGNESIA.—*Magnesium oxide; magnésie, magnésium oxyde, magnésie blanche*, French; *magnesia, magnesium-oxyd, talkerde, bittererde*, German. Symbol, MgO.

Magnesium oxide is a fine, light, white powder, tasteless and inodorous. It requires for its solution 5000 parts of water at 60° Fahr. (15°·5 C.) and 36,000 parts at 212° Fahr. (100° C.). Its specific gravity ranges from 3·07 to 3·2, and is increased by prolonged ignition to 3·61 (ROSE). It is fusible by the heat of the oxyhydrogen blowpipe, when it forms an enamel sufficiently hard to scratch glass. It is not caustic, yet perfectly neutralizes all acids. It attracts carbonic acid from the air, though very slowly, forming magnesium carbonate.

Magnesia changes the colour of the purple infusion of red cabbage to a bright green, reddened litmus solution to blue, and yellow turmeric to brown.

Magnesia is produced when magnesium is burnt in air or in oxygen. Commercially it is obtained by ignition of the carbonate, or by precipitation as hydrate from solution of the sulphate by potassium or sodium hydrate. MgH_2O_2, the hydrate of the oxide, occurs native as brucite in rhombohedral forms. The oxide can be crystallized in cubes and regular octahedra by igniting the amorphous magnesia in a stream of hydrochloric acid gas.

Magnesia is a valuable medicine; as an antacid it is as efficacious as the alkalies, whilst, unlike them, it is not caustic.

The most delicate test for magnesia in solution is to add first ammonium carbonate, then sodium phosphate, when a dense crystalline powder precipitates, having the composition $Mg(NH_4)PO_46H_2O$; if the solution is dilute the precipitation is much promoted by stirring.

DEVILLE states that magnesia prepared by ignition of the nitrate is converted, by prolonged immersion in water, into a hydrate (MgH_2O_2) much resembling marble, but harder and more translucent. A similar hydrate is formed by heating the chloride. The ignition must not exceed a dull red heat; by exposure to a white heat for twelve hours magnesia loses altogether the property of hardening when hydrated.

H. SCHWARZ has succeeded in manufacturing a like hydrate from the native carbonate ($MgCO_3$) by igniting it at the lowest possible temperature consistent with the evolution of the carbonic acid. The paste made by mixing this oxide with water hardens in about twelve hours, and afterwards by prolonged immersion becomes as hard as the best Portland cement.

SORREL states that a mixture of magnesia with concentrated solution of magnesium chloride (specific gravity 1·1 to 1·2) hardens in a short time, and becomes an eminently useful hydraulic cement. The paste thus made is capable of binding 20 times its weight of sand. Calcium chloride may be substituted for the magnesium chloride with good effect.

Magnesium Carbonate, $MgCO_3$.—This salt of magnesium occurs native, in rhombohedral crystals, as

magnesite; it is found in Piedmont, Moravia, North America, &c., associated with *serpentine* and the native hydrate. It is also found in combination with carbonate of lime; indeed, most of the calcareous rocks contain magnesium carbonate. The species of marble called *dolomite* contains about 40 per cent. of magnesium carbonate.

The anhydrous magnesium carbonate is isomorphous with calcium carbonate; when moistened with water it gives an alkaline reaction with litmus and turmeric. It is infusible before the blowpipe, and dissolves slowly in acids with but little effervescence.

Alkaline carbonates do not precipitate anhydrous magnesium carbonate from solutions of magnesium salts, but an hydrated carbonate: this can, however, be dehydrated by passing a stream of carbonic acid through a mixture of the washed precipitate with water, until it is completely dissolved, and then evaporating the liquid to dryness. $MgCO_3$ is then obtained as a crystalline powder, having the form of arragonite ($CaCO_3$). If the solution be left to evaporate spontaneously crystals deposit, having the composition $MgCO_3 + 3H_2O$. The same hexagonal crystals are deposited from a mixed solution of magnesium sulphate and potassium and sodium sesquicarbonate.

The solution of magnesium carbonate is sold extensively as *soluble magnesia*, or *bicarbonate of magnesia*.

When an alkaline carbonate is poured into a solution of a salt of magnesia, a white gelatinous precipitate is formed, which is a hydrated magnesium carbonate, or a combination of the hydrate and of the carbonate. The proportions of these two compounds vary according to the quantity of alkaline carbonate employed, the strength of the solutions, and the temperature. This product is made in large quantities in pharmaceutical chemistry, and is the *magnesia alba* of the pharmacopœia. Two kinds, identical in composition, are prepared, namely, the *light* and the *heavy*. For *heavy* magnesia, add one volume of a cold saturated solution of sodium carbonate to a boiling mixture of one volume of a saturated solution of sulphate of magnesia, and three volumes of water; boil until effervescence has ceased, constantly stirring with a spatula; then dilute with boiling water, set aside, pour off the supernatant liquor, and wash the precipitate with hot water on a linen cloth; afterwards dry it by heat in an iron pot. *Light* magnesia is prepared by employing dilute solutions of the sulphate of magnesia and carbonate of soda. If no heat be used, it is apt to be gritty.

A heavy granular magnesia is prepared by separately dissolving 12 parts of magnesium sulphate, and 13 parts of crystallized sodium carbonate, in as small a quantity of water as possible, mixing the hot solutions, and washing the precipitate.

The light magnesium carbonate is prepared as follows:—A solution of 100 parts of sulphate of magnesia in 100 of water is put into a vat heated by steam; a solution of 125 parts of crystallized carbonate of soda is quickly stirred into it, and the temperature raised to 176° Fahr. to expel carbonic acid, which holds some of the magnesia in solution; the liquor is then decanted, and the precipitate is washed three times with lukewarm water, free from salts of lime. It is then transferred to linen strainers, and allowed to drip from twenty-four to forty-eight hours, and is transferred to cubical boxes without bottoms, placed upon a table of plaster or porous stone, which quickly absorbs the water: after some time the boxes are turned, so as to present the upper side of the magnesia to the absorptive surface; the drying is completed in warm rooms.

The carbonate of magnesia of commerce is likewise obtained in various ways from bittern. It is also separated from magnesian limestone by a process adopted by Pattison, which consists in calcining it at a dull red heat, by which only the magnesian carbonate is decomposed; the calcined stone is then diffused through water, and subjected to the action of carbonic acid under pressure, by which the magnesia alone is dissolved, and is afterwards obtained by rapidly boiling down the solution. It is a beautiful white substance, very light, and without taste or smell. It dissolves in 2500 parts of cold, and in 9000 parts of hot water.

Magnesium Citrate $(C_6H_5O_7)_2Mg_3 + Aq.$—This salt is prepared by saturating a solution of citric acid with magnesium carbonate. It is white, pulverulent, tasteless, and very soft to the touch, heavier than magnesia, and when a slight excess of citric acid is present, is readily dissolved by water.

Magnesia, Granular Effervescent Citrate of.—This popular saline does not contain citrate of *magnesia*, as its name implies; but is essentially a kind of lemon and kali in a granular form, with or without a minute quantity of *sulphate* of magnesia (Epsom salt). A solution of the granules in water contains, after the effervescence is complete, tartrate and citrate of soda and sugar.

The following is the process for preparing this compound followed by one of the largest manufacturers:—16 parts of bicarbonate of soda, $10\frac{1}{2}$ of tartaric acid, 4 of citric acid, from 8 to 18 of sugar, half of sulphate of magnesia, and 2 parts of crystallized bisulphate of soda, are intimately mixed by sifting, and placed to a depth of not more than half an inch on a hot zinc, tin, or enamelled iron plate. In a few minutes the mixture becomes spongy from the formation of carbonic acid gas, when it is worked about and turned over with a scoop or other convenient instrument, to prevent any of the particles from becoming too dry. In a minute or two more the mass is thrown on a cold slab, and put through a sieve of four to six meshes to the square inch. It is again heated and sifted through a rather finer sieve to separate the dust, and finally further heated till desiccation is complete.

Some manufacturers replace a portion of the citric by an equivalent quantity of tartaric acid, and omit the Epsom salt. Others add as a flavouring agent a little essence of lemon.

A solution of the *true* citrate of magnesia may be readily prepared in an effervescent form, by adding to a large wine-glassful of *fluid* magnesia, two teaspoonfuls of lemon juice, or a solution of citric acid.

MAGNESIUM SULPHATE; *bitter salt*, *sal anglicum*, *sal seidlitzense*, *sal catharticum*, *sal amarum*, *Epsom salts*, *Epsomite*. $MgSO_4,7H_2O$.

This salt is found in sea water, and in many mineral waters—such as those of Seidlitz, Leydschutz, Egra, and Epsom, in Surrey. It is largely manufactured from dolomite (native carbonate of magnesia), by treating it with sulphuric acid. The dolomite is calcined, and reduced to powder by being sprinkled with water while still hot; it is then diffused through a large bulk of water, and strong oil of vitriol added. Calcium sulphate and magnesium sulphate are formed; as the former is almost insoluble in water, while the latter is extremely soluble, they are readily separated.

Magnesium sulphate, besides being used as a purgative and for agricultural purposes, is manufactured on a very large scale for the use of warp sizers. Manchester alone uses something like 150 tons weekly. The present method of making it from magnesite (magnesium carbonate) is described by J. H. SWINDELLS.

The plant required consists of—

1. A digester, a square wooden box, lined with thick sheet lead; on the bottom and about 3 feet up the sides Yorkshire flags are placed, so as to protect the lead from the effects of blows from the magnesian limestone, which often shakes about very much. This digester is made of various sizes.

2. A settler, made either of lead or flags well cemented together. The use of iron should be avoided. The settler may be made as large or larger than the digester.

3. An iron evaporating pan, heated by steam or a fire.

4. Coolers. These are generally made of wood. J. H. SWINDELLS recommends them to be made of slate or flags. He thinks one large shallow slate cooler is better than several small deep ones.

5. A drainer. This is a large vessel with a false bottom for draining the salts. It may be made of wood, and of any shape.

6. A stove room for drying the salts. This contains shelves of any width, placed about 18 inches apart. The stove is heated by means of steam passing through pipes running along the floor.

7. A "washer" for washing the "settlings" of the "drainer."

8. A steam boiler.

This may be considered the whole of the manufacturing plant.

Supposing the digester is 6 feet square and 7 feet deep, the process is begun by placing therein about 3 tons of magnesian limestone. Twelve ordinary carboys of sulphuric acid are then emptied into the digester, and water added until the liquor has a specific gravity of 1·125 or 1·150. The dilute acid is allowed to act upon the stone for about an hour without being aided by heat; at the end of this time the action slackens, and steam from the boiler is supplied to quicken it. A lead pipe of about three-quarters of an inch bore is made to go about half way down the digester, and through this pipe steam is forced into the liquor. From eight to twelve hours is the usual time taken to neutralize a "batch."

When sufficiently neutral, the liquor in the digester will stand from 40° to 50° on TWADDELL's hydrometer. It is then run off by means of a tap or plug into the settler. If the liquor happens to show a trace of acid it is neutralized, and any iron present precipitated by any of the known means. "Settling" occupies from three to four hours. The clear liquor is then siphoned off into the evaporating pan.

The same process is gone through with successive batches, until sufficient liquor has been obtained for a "boiling," care being always taken to keep the liquor free from acid. Indeed, working on the alkaline test may be said to answer best.

The liquor in the boiling down pan is evaporated till it stands 66° Twaddell. When this point is reached the steam (if used) is turned off, and the liquor allowed to remain undisturbed for a few hours, so as to allow all floating and suspended particles to settle down. The liquor should be perfectly clear before it is run off.

When sufficiently settled the solution is conveyed to the cooler or coolers, and agitated at certain intervals, to make the salt fall in small crystals. When the salt has finished falling, the mother liquor is run off and pumped into the evaporating pan. New liquor from the digester is added, and the same process, already described, is gone over again. The salt is taken from the coolers and allowed to drain. It is then placed on the shelves of the stove room, and dried at a temperature not above 80° Fahr. When sufficiently dry it is sifted (sometimes crushed), and placed in casks for the market.

The "settlings" from the "drainer" are placed in the "washer" and washed, and the liquor is allowed to filter through, after which it is pumped into the evaporating pan with the other liquor.

This may be said to be the whole process, the object aimed at being to make sulphate of magnesia pure, and especially free from iron.

When used by warp-sizers it is for the purpose of adding weight to the cloth.

Epsom salts are also made from the bittern or mother liquor remaining after the evaporation of sea water, and the separation of the chloride of sodium therefrom. The liquor is boiled for some hours in iron pans. During the ebullition, some chloride of sodium deposits. The lighter impurities are separated by skimming, and the strong solution is removed into wooden refrigerators, where, in a day, one-eighth part of crystals of sulphate, called *single Epsom salts*, or *singles*, are deposited. These are drained, dissolved, and recrystallized; they are then termed *double Epsom salts*, or simply *doubles*.

At Monte della Guardia, near Genoa, sulphate of magnesia is prepared from schistose minerals containing sulphur, magnesia, copper, and iron. The ores, after roasting, are converted into sulphates by moistening and exposure to air. They are then lixiviated, and the solution is deprived, first of copper by refuse iron, and afterwards of iron by

lime. At Baltimore sulphate of magnesia is procured from the silicious hydrate of magnesia or *marmolite*, by reducing the mineral to powder, saturating with sulphuric acid, and calcining the dried mass to convert the iron into ferric oxide. It is then redissolved in water, heated with sulphide of calcium to remove the remaining iron, and crystallized. By a second crystallization it is obtained nearly pure.

A very large quantity of sulphate of magnesia is manufactured at Newcastle-upon-Tyne. It is made from magnesian limestone, by calcination and washing to separate the lime, and subsequent addition of sulphuric acid.

The carbonic acid produced by the action of the sulphuric acid is sometimes employed in the manufacture of bicarbonate of soda. The mixed sulphates of lime and magnesia are thrown into large wooden vessels, fitted with a false bottom. Water is now poured upon the thick mass, and drawn through by the action of a pair of pumps, worked from an engine shaft in any convenient manner. In this way the whole of the sulphate of magnesia is extracted with small expenditure of water; and the solution, after being pumped into a reservoir, is allowed to filter through layers of sandstone and charcoal, to render it clear and bright. The liquor is now concentrated by evaporation, and made to crystallize as rapidly as possible, in shallow wooden troughs lined with lead, in order that the crystals may be as small as possible, to meet the prejudice of the trade in this respect. The sulphate of lime left on the filter or false bottom is worked up in the manufacture of Venetian red.

In the manufacture of alum as conducted near Whitby, the *salts' mothers* by crystallization yield a crude sulphate of magnesia, called Rough Epsoms, and having the following composition:—

Sulphuric acid,	32·26
Magnesia,	15·35
Ferrous oxide,	1·73
Oxides of nickel and cobalt,	0·12
Lime,	0·09
Alumina,	1·33
Potash,	0·83
Water,	48·29
	100·00

These rough Epsoms are mixed with magnesian lime in such proportions that all the sulphuric acid, except that in combination with the potash and magnesia, is taken up by the free alkaline earths. The mixture is then calcined in an ordinary reverberatory, at a dull red heat. The calcined product is afterwards thrown into a large circular cistern filled with water, and in which a pair of edge-stones are made to revolve by suitable machinery. By this arrangement the large pieces are ground to powder, while the agitation produced by the motion of the edge-stones facilitates the solution of the Epsom salt.

The sulphate of magnesia liquor is subsequently clarified in the manner previously described, and crystallized in the usual shallow pans.

STEATITE, *soapstone*, contains silica, magnesia, alumina, oxide of iron, oxide of manganese, and water. It is found in North America, Sala in Sweden, Cornwall, and China. It is employed in polishing articles made of serpentine, marble, sulphate of lime, and plate-glass; it is also sometimes used as a substitute for grease for the axles of carriages. It is further used for sketching in outline on silk, linen, and glass; as crayon; for painting on glass, and for removing stains in woollen and silk goods. It has also been added in some cases to the materials for porcelain, to improve the transparency, but it renders the mass much more brittle. The apparatus employed for the production of chlorine is occasionally manufactured from this material, as it resists the corrosive action of that gas.

MEERSCHAUM, employed in manufacturing the celebrated tobacco pipes, contains:—

	Levant. Lychnell.	Madrid. Berthier.	Natolia. Thomson.
Silica,	60·87	53 80	42·00
Magnesia,	27·80	23·80	30·50
Lime,	—	—	2·30
Alumina, Ferric oxide,	0·09	1·20	2·00
Water,	11·24	20·00	23·00
Loss,	—	1 20	·20
	100·00	100·00	100·00

MEERSCHAUM FROM MOROCCO ANALYZED BY DAMOUR.

Silica,	55·00
Magnesia,	28·00
Alumina,	1·20
Ferric oxide,	1·40
Lime,	1·00
Potash,	·52
Water,	10·35
Sand,	2·50
Loss,	·03
	100·00

ASBESTOS.—This material is of frequent use in the laboratory, and in the manufacture of various articles intended to resist the action of fire, such as lampwicks, &c. Annexed is its composition:—

	Kobell.	Richardson.	Thomson.
Silica,	43·50	43·25	40·95
Magnesia,	40·00	33·85	34·70
Ferric oxide,	2·08	10·90	10·05
Alumina,	·40		1·30
Water,	13·80	7 00	12·00
Loss,	·22	5·00	1·00
	100·00	100·00	100·00

A mixture of asbestos with a small quantity of paper pulp has lately been made into sheets of about the $\frac{1}{16}$th of an inch in thickness, and found to resist the action of moderately high temperatures very well; being plastic it can be cut and moulded into a variety of useful shapes for laboratory uses.

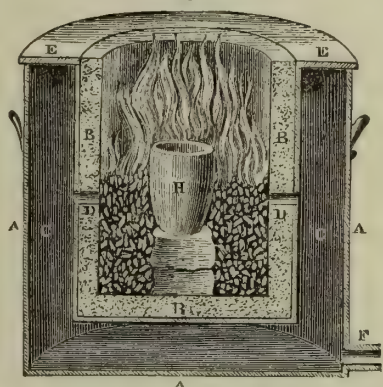
MANGANESE—*Manganèse*, French; *Mangan*, German; *Manganum*, Latin. Symbol, Mn. Atomic weight, 55.—The black mineral known in commerce by the name of manganese—*braunstein*, German—has long been employed to counteract the green tint of glass. It was formerly called *magnesia nigra*, from its resemblance to the magnetic oxide of iron, or loadstone. A mine of this mineral was discovered in England by BOYLE. Some experiments were made upon it by GLAUBER in 1656, and by WAIZ in 1705; but chemists do not appear to have

directed particular attention to it until a later period. Mineralogists agreed in classing it among the ferruginous ores until Pott, in 1740, showed that it often contains mere traces of iron; after which, on the supposition that it consisted chiefly of a peculiar earth, a separate place was assigned to it in treatises on mineralogy. This hypothesis was in the year 1774 distinctly proved to be correct, by the elaborate researches of Scheele and Bergman. Gahn subsequently showed that this earthy base contained a metal, not hitherto isolated, upon which he bestowed the appellation of *magnesium*. As, however, this term was afterwards employed to distinguish the metallic base of magnesia, it was superseded by the designation now in use. The metal manganese, owing to its powerful attraction for oxygen, does not occur in a free state in the earth's crust; but its mineral oxides are abundant, and are extensively employed in the arts—chiefly in the manufacture of glass and pottery, and in the preparation of chlorine for the production of bleaching powder.

Preparation.—From the difficulty of its isolation, metallic manganese has not been rendered available for any useful purpose. The processes for its reduction are generally conducted on a small scale, in the laboratory. Like iron and cobalt, it is very difficult to be obtained in a state of absolute purity. It is necessary, in the first place, to procure a pure oxide of manganese, which may be effected by any of the following processes:—The common black oxide of manganese of commerce is digested for some time with dilute hydrochloric acid, washed, in order to free it from carbonate of lime, and then heated with strong hydrochloric acid. During the solution of the mineral, chlorine gas is abundantly disengaged, and when the action is complete the solution contains chloride of manganese and sesquichloride of iron. The liquor, after filtration, is evaporated to dryness in a porcelain basin, and the dry residue is strongly heated, with constant stirring, until it assumes an ash-grey hue, and no longer evolves acid fumes. By this treatment the chloride of iron is in part volatilized, and in part converted into sesquioxide of iron and hydrochloric acid. The residue is now digested with water, the solution filtered, and carbonate of soda, in slight excess, added to the liquid. The precipitated carbonate, after washing and drying, is ignited in a covered crucible, when it furnishes a pure oxide; or the solution in hydrochloric acid is diluted with water, and treated with repeated quantities of carbonate of soda, with continued digestion and stirring, until the liquid, rendered clear by subsidence or filtration, gives a pure white precipitate with a further quantity of carbonate of soda, showing that all the oxide of iron has been precipitated. This having been attained, the whole solution is freed by filtration from the precipitate, and the clear liquid precipitated by carbonate of soda in excess.

Faraday recommends the following process for the preparation of pure protochloride of manganese:—Finely-powdered and strongly-calcined black oxide, previously cleansed from carbonate of lime, is ignited with half its weight of chloride of ammonium, beginning with a moderate heat, and gradually raising the temperature to low redness. The chloride of manganese formed is dissolved out, and the solution filtered. The pure oxide of manganese, prepared by the process already indicated, is moistened with oil and heated to redness several times; then made into a thick paste with oil, introduced into a charcoal-lined crucible, covered with charcoal powder, and a lid luted on the mouth of the crucible, which is afterwards exposed for two or three hours to the strongest heat of a smith's forge or a powerful blast furnace. Sefström's apparatus, represented in Fig. 1, is commonly employed for the reduction. In a cylindrical iron case, A, is placed a second cylinder, B, lined with

Fig. 1.



fire-brick. The crucible, H, is arranged as represented in the drawing, and surrounded with glowing charcoal or coke. The blast is admitted at F into the space, C, which intervenes between the two cylinders, from which, after becoming considerably heated, it is forced into the fire-chamber through a series of openings, D D. The metal collects in the form of a button at the bottom of the crucible.

Properties.—Metallic manganese, as thus obtained, contains some carbon; it presents a greyish-white colour without much lustre, and a fine granular texture. It is rather soft and brittle, and is readily split or broken. Its specific gravity is stated by John to be 8·013. Its equivalent is 55. When pure it is not attracted by the magnet. It is exceedingly difficult of fusion, requiring for liquefaction the most intense heat of a wind furnace. The manganese prepared by the process described is always contaminated with carbon and silicium, and resembles, therefore, common pig or cast iron. On subjecting the metal to fusion with borax, the carbon is separated, and the regulus becomes more fusible; but it is probable that the product in this case contains boron or sodium. Manganese readily tarnishes by exposure to the air—hence, like potassium, it must be kept under naphtha. When heated to redness in open vessels, it absorbs oxygen with rapidity. It decomposes water slowly at common temperatures, with disengagement of hydrogen gas; but at a red heat oxidation is very rapid. It also dissolves

readily in dilute acids, with escape of hydrogen. By fusion at a high temperature, manganese may be alloyed with various other metals. A compound of about 4 equivalents of manganese and 1 equivalent of iron was produced in considerable quantity by Buttray, in a furnace employed for fusing cast-steel. This alloy became only slightly tarnished when freely exposed to the air, and did not affect the magnetic needle. When manganese is combined by fusion with 6 or 7 per cent. of silicium, a regulus results which possesses the appearance of the ordinary metal, but differs much from it in its chemical characteristics; it does not oxidise even at a red heat, and withstands the action of nitro-hydrochloric acid.—Sefström.

Berzelius expressed the opinion that the presence of the small proportion of silicium is not sufficient to account for this total change of properties, and that there must exist in the compound or alloy an allotropic modification of the metal, the alteration being effected or induced by the presence of the silicium at a temperature at which it would not occur with manganese alone.

C. Brunner prepared metallic manganese by acting upon the fluoride with half its weight of sodium, the process being similar to that employed for the reduction of aluminium. Deville procured pure manganese by reducing pure manganic oxide with an insufficient quantity of sugar charcoal in a lime crucible. Manganese thus obtained possesses properties essentially different from those usually attributed to this metal. Its colour is like that of some cast iron. It is brittle and very hard, not yielding to a steel file; but, on the country, scratching the best-tempered steel. It is capable of the most perfect polish. It is not altered even in moist air at the ordinary temperature. When heated it acquires nearly the same colours as steel, passing afterwards to brown, by covering itself with a layer of oxide. The specific gravity of different specimens varied from 7·138 to 7·206. It is not attracted by the magnet even when in powder, and has no influence on the magnetic needle. Acids attack it violently, even in the cold.

The alloys which it forms, with the exception of ferro-manganese, have not received any extensive applications, although some of them are both malleable and ductile. Perhaps the most remarkable are the alloys with copper and zinc, which are similar in appearance to German silver, and can be rolled both hot and cold, whereas German silver can only be rolled cold. The principal objection to their application seems to have been the cost of metallic manganese; but this objection has been to a great measure overcome by Hugo Zamin's process of making cast manganese direct from manganese ore.

Zamin makes use of two fluxes, which he calls respectively white flux and green flux. His white flux consists of—

Ground glass,	63 parts.
Quick lime,	18½ "
Fluor spar,	18½ "

His green flux is made by fusing together—

White flux,	34 parts.
Lamp black,	5½ "
Manganese ore (rich),	60½ "

The produce of this fusion is 17½ parts of cast manganese, and a slag of an olive green colour which is saturated with protoxide of manganese, and constitutes his green flux. Having obtained the green flux, Zamin makes cast manganese by mixing 1000 parts of manganese ore with 91 of lamp black and 635 of green flux, and finally adds enough oil to moisten it. This mixture is heated in a graphite crucible protected from oxidation by a round cover of thick wood placed over it, and the crucible is covered with a fire-clay or plumbago lid, which is luted on, with the exception of a small opening for the escape of gases. This mixture yields a green slag and 420 parts of cast manganese, which, in the case of an ore containing 50·5 per cent. of manganese and 3·5 per cent. of iron, was found to have the following composition:—

	Per Cent.
Manganese,	96·900
Iron,	1·050
Aluminium,	·100
Calcium,	·050
Phosphorus,	·050
Sulphur,	·050
Silicon,	·850
Carbon,	·950
	100·000

This cast manganese, after being reduced to coarse powder and purified by fusion with one-eighth of its weight of carbonate of manganese, was found to have the following composition:—

	Per Cent.
Manganese,	99·910
Iron,	·050
Silicon,	·015
Carbon,	·025
Other substances,	traces
	100·000

Oxides.—Manganese forms at least five distinct compounds with oxygen, besides several compound oxides. The composition of these oxides is exhibited in the following table:—

Protoxide, or manganous oxide,	MnO.
Sesquioxide, or manganic oxide,	Mn_2O_3.
Binoxide, or peroxide — black oxide,	MnO_2.
Manganoso-manganic oxide — red oxide,	Mn_3O_4 or MnO,Mn_2O_3.
Varvicite,	Mn_4O_7, or $Mn_2O_3,2MnO_2$.
Manganic anhydride,	MnO_3.
Permanganic anhydride,	Mn_2O_7.

Of these the first only possesses marked basic properties; the sesquioxide is a very feeble base; and the two compounds at the bottom of the list are, as their names indicate, anhydrous acids. The protoxide is readily obtained by heating the oxalate in a covered crucible, or in a glass tube closed at one end. When a caustic alkali is added to a solution of chloride or sulphate of manganese, the hydrated oxide falls as a flocculent white precipitate, which rapidly acquires a dark tint on exposure to the air. Binoxide of manganese may be prepared by passing

chlorine gas through a solution of the acetate. Sesquioxide of manganese is produced when the binoxide is kept for a considerable time at a moderate red heat. It also occurs in nature as *braunite* and *manganite*. The red or manganoso-manganic oxide is always produced when any of the higher oxides is exposed to a white heat, either in closed or open vessels, or when hydrated protoxide is exposed to the air. It is the most permanent of all the oxides of manganese; it is not affected by exposure to any temperature, while all the other oxides readily pass into it, under the influence of heat. When finely powdered it is brownish-red while cold, and nearly black while warm. When fused with borax or glass, it communicates to these bodies a beautiful violet or amethyst tint, a character by which manganese may readily be detected before the blow-pipe. Many coloured minerals—for example, the amethyst—owe their tint to the presence of this oxide. Manganate of potash is readily produced by fusing binoxide with carbonate or hydrate of potash, with or without the addition of chlorate. The compound has a fine green colour. Upon the ready formation and great colouring power of manganic anhydride, E. Davy has founded an elegant method for the detection of manganese. The substance is heated on silver foil, with a drop of a strong solution of caustic potash, and the dry residue is gently ignited, when it will exhibit, if manganese be present in appreciable quantity, a very distinct green colour. When compounds of manganese are heated before the blow-pipe with carbonate of soda, on a loop of platinum wire, a green bead is obtained, manganate of soda being formed. Manganate of potash has received the name of *chameleon mineral*, from the circumstance that the dark-green solution obtained by digesting it in a small quantity of cold water, assumes various shades of colour on being diluted, the ultimate result being a liquid having a fine carmine-red tint. The change of tint, which is induced more readily by the addition of an acid, is owing to the resolution of the manganic into permanganic acid, which remains in solution, and binoxide of manganese, which falls as a precipitate.

$$3MnO_3 = Mn_2O_7 + MnO_2.$$

Crum's test for manganese depends upon the formation of permanganic acid. The compound under examination is dissolved in a little nitric acid, and binoxide of lead added, when the fine red tint of permanganic acid will be communicated to the liquid. Solution of permanganate of potash is much employed in the German and French laboratories as an oxidising agent: in this country the bichromate is more generally used. The solution is best prepared by the method recommended by Gregory: 4 parts of finely pulverized binoxide of manganese, and $3\frac{1}{2}$ parts of chlorate of potash, are intimately mixed together, and added to 5 parts of hydrate of potash dissolved in a small quantity of water. The mixture is evaporated, and the residue completely dried, pulverized, and exposed to a low red heat in a platinum crucible. The agglutinated mass is again powdered and added to a considerable quantity of boiling water, and the solution allowed to settle. When clear it is decanted, and is ready for use. It is quite permanent when preserved in well-stoppered bottles.

All the higher oxides of manganese are reduced to the condition of proto-compounds by the action of warm sulphuric or hydrochloric acid, with the elimination of oxygen or chlorine, as the case may be. The following equations represent the action of hydrochloric acid upon the binoxide, the sesquioxide, and the red oxide of manganese:—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_4$$
$$Mn_2O_3 + 6HCl = 2\,MnCl_2 + 3H_2O + Cl_2$$
$$Mn_3O_4 + 8HCl = 3\,MnCl_2 + 4H_2O + Cl_2$$

Protoxide of manganese is a powerful base of the magnesian class. Its salts are sometimes quite colourless; but they frequently possess a pink shade, probably from the presence of traces of permanganic acid, or oxide of cobalt. The soluble salts are nearly neutral, and when dissolved exhibit the following reactions:—

Caustic potash,	A white precipitate of hydrated protoxide, which becomes brown by the absorption of oxygen.
Ammonia,	Do.
Alkaline carbonates and bi-carbonates.	White precipitate.
Ferrocyanide of potassium,	Do.
Sulphuretted hydrogen,	No effect in acid solutions.
Ammonium sulphide,	A flesh-coloured precipitate.

For the detection of minute quantities of manganese, especially when mixed with other metals, Crum's test, already detailed, is probably the most delicate.

Ores.—The compounds of manganese which occur native are numerous, but as those only are of importance in the arts which consist solely or chiefly of one of the higher oxides, the minerals which come under consideration in this place are comparatively few in number.

Pyrolusite is the name applied to the native binoxide in its anhydrous and crystallized state. It is chiefly this variety that is employed by the glass-makers, while *wad* and other less pure ores are consumed in the elimination of chlorine from hydrochloric acid or sodium chloride. The crystalline form of pyrolusite is the rhombic prism, and it generally occurs in the form of minute crystals grouped together, and radiating from a common centre. It has the same form as *manganite*, which consists of hydrated sesquioxide, and appears to be formed from that mineral by absorption of oxygen and loss of water, some masses of crystals having been observed to consist of pyrolusite externally and manganite internally. Pyrolusite has an iron-black or dark steel-grey colour, and a metallic lustre. It is not very hard; its specific gravity is 4·7 to 4·97. It frequently contains *manganite*, *psilomelane*, sesquioxide of iron, alumina, silica, baryta, carbonate and sulphate of lime, and occasionally, according to Phillips, traces of calcium chloride. The following analyses of specimens of pyrolusite are by Turner:—

	Elgersburg.		Ihlefeld.
Binoxide of manganese,	97·84	....	97·22
Baryta,	·53	....	·66
Silica,	·51	....	·55
Water,	1·12	....	1·57
Calcium chloride,	—	....	traces
	100·00		100·00

This valuable ore is extensively worked in Ilmenau, Elgersburg, and various other districts in Thuringia; and the mines at Vorderschrensdorf, in Moravia, yield annually many hundred tons. It has also been found in several localities in America and elsewhere.

Name of Ore.	Locality.	Composition.							Analyst.	= MnO_2.
		Binoxide of Manganese.	Sesqui-oxide of Manganese.	Sesqui-oxide of Iron.	Baryta.	Lime.	Clay.	Water.		
Wad,	Grorio, Mayenne,	64·2	11·0	6·0	—	—	3 0	15·8	Berthier.	70·2
"	Viodessos,	54 6	26·0	7·0	—	—	—	12·4	"	68·9
"	Graubundten,	22·6	31·0	3·6	—	—	Quartz 35·6	8·8	"	39·6
"	Upton Pyne, Devon,	61·7	26·2	—	1·4	—	—	10·7	Turner.	76·1
"	Ilmenau,	51·6	27·0	1·0	8·1	—	Silica. 2·5	9·8	Scheffler.	66·4
"	Rubeland,	66·0	15·0	1·0	·3	And KO. 6·9	·5	10·3	Rammelsberg.	74·2
Ochrey Wad,	"	73·3	23·6	—	trace	—	—	3·1	Turner.	86·3
Varvicite,	Warwickshire,	50·	45·	—	—	—	—	5·	"	74·7
Psilomelane,	Schneeberg,	54·5	22·7	—	16·4	—	·2	6·2	"	66·0
"	Baireuth,	74·3	17·0	—	—	Potash. 4·5	—	4·2	Fuchs.	83·6
Braunite,	Elgersburg	—	96·8	—	2·3	—	trace	9	Turner.	53·2
Manganite,	Ihlefeld,	—	89·9	—	—	—	—	10·1	"	49·4
Hausmannite,	"	Prot-oxide. 30·7	68·3	—	·1	—	·4	·5	"	37·5

Wad is the native hydrated binoxide. It is this ore that is commonly employed in the preparation of chlorine. It is tolerably abundant, and is found in England, Ireland, Sweden, Germany, and America; it appears generally in the form of brownish-black masses, or loosely agglomerated brown scales. Some varieties are hard and compact, and difficult to pulverize; others are comparatively soft and ochrey. Wad consists essentially of hydrated binoxide of manganese, $MnO_2.H_2O$, but it is always more or less mixed up with manganic or manganoso-manganic oxide, and generally with variable quantities of sesquioxide of iron, clay, quartz, baryta, carbonate of lime, &c. Some specimens contain much oxide of cobalt, and a few contain oxide of copper. Analyses of specimens of wad from various localities, and of other ores of manganese capable of being applied to economic purposes, are exhibited in the preceding table. The last column of the table shows the amount of pure binoxide corresponding with the quantity of chlorine yielded by 100 parts of the ore.

Psilomelane is one of the most generally diffused ores of manganese. It is compact and fibrous; specific gravity 4 to 4·328; rather hard. It has a dark steel-grey colour, and submetallic lustre; it generally occurs in botryoidal masses.

Braunite is met with in octohedral crystals, and also massive; it is commonly nearly pure sesquioxide of manganese. *Manganite*, or grey manganese ore, is the hydrated sesquioxide, $Mn_2O_3.H_2O$, and is generally very pure, and therefore well adapted for the manufacture of glass. It occurs in rhomboidal prisms, and also in columnar and granular masses. It is moderately hard; specific gravity 4·3 to 4·4; colour between iron-black and steel-grey, with a submetallic lustre. It is found at Ihlefeld in the Hartz, in Aberdeenshire, Bohemia, Saxony, and other localities.

Uses.—The most important applications of manganese ore in the arts are the production of chlorine and the decoloring of glass. Although, in the manufacture of glass, the purest materials are employed, yet traces of iron compounds are invariably present in one or more of the materials, giving to the product a very faint but distinct green, olive, or yellow tint, according to the state of oxidation of the metal. The cautious addition of black oxide of manganese destroys or conceals the objectionable tint. Its action was formerly supposed to be merely the oxidation of the green protoxide of iron to the faint yellow sesquioxide; but Liebig has suggested that the effect is not chemical but optical, and that the amethyst colour communicated by the red oxide of manganese counteracts the yellow or greenish-yellow tint of the oxide of iron. This is probably the correct explanation of the action, since other oxidising agents, red oxide of lead for example, do not produce the desired effect. Chemists employ the binoxide of manganese for the preparation of oxygen and chlorine gases, and it is employed, in conjunction with dilute sulphuric acid, as an oxidising agent in organic chemistry.

Binoxide of manganese has been employed for increasing the siccative quality of linseed oil; and the artificial binoxide, mixed with the same oil, has been recommended as a black paint, which may be used with advantage for the manufacture of printers' ink.

Of the numerous combinations of manganese with the halogens, and of the oxides with acids, the acetate, protochloride, and the sulphate of the protoxide are the only compounds which are manu-

factured on the large scale or applied to economic purposes, and are consequently sufficiently important to claim consideration in a work on technology.

Acetate of Manganese.—A full description of this salt is given in the article Acetic Acid.

Chloride of Manganese.—A solution of this compound in a state of purity is most readily obtained by the method recommended by Faraday, already detailed, or by digesting a solution of purified black oxide of manganese in hot and strong hydrochloric acid, with carbonate of manganese, until all the sesquioxide of iron is displaced and thrown down. When the solution is highly concentrated by evaporation, it yields crystals of the hydrated salt, MnCl,4HO. These crystals are highly deliquescent, and dissolve in two-thirds of their weight of water at 60°, and in a much smaller quantity at a higher temperature. The salt may be rendered anhydrous by the application of the heat of a spirit flame, while inclosed in a glass tube through which a current of dry hydrochloric acid gas is made to pass. It is a rose-coloured crystalline mass.

Chloride of manganese is a refuse or waste product in chemical factories where chlorine is prepared from manganese and hydrochloric acid. It has been employed in the purification of coal gas. It may be used in dyeing for the production of *manganese brown*, but the sulphate is generally employed for this purpose. A crude solution of chloride of manganese, neutral and free from iron, may be prepared by digesting the refuse menstruum already referred to with powdered chalk, which decomposes the sesquichloride of iron, but does not affect the manganese salt.

Sulphate of manganese is obtained in transparent, slightly rose-coloured crystals, by dissolving the pure carbonate in dilute sulphuric acid, and concentrating by spontaneous evaporation. The crystals have the form of sulphate of copper, and a similar composition, $MnSO_4 + 5H_2O$; but by evaporation and crystallization at various temperatures, crystals with greater and less proportions of water may be obtained. The crystals are remarkably soluble in water.

This salt is prepared on a considerable scale for the use of the dyer and calico printer. The mode of preparation generally adopted is as follows:—Black oxide of manganese is ignited with a small quantity of charcoal powder, in order to reduce it to the state of protoxide. This product being now treated with moderately dilute sulphuric acid, a crude sulphate is obtained containing a considerable proportion of sulphate of iron, to get rid of which the solution is boiled down to dryness, and the residue ignited or roasted. The mass is digested with water, when the manganese salt dissolves, while the iron remains insoluble as a basic sesquisulphate. The salt is obtained from the solution by evaporation. Another mode of preparation is to ignite a mixture of black oxide of manganese and sulphate of iron, then to digest in water, and evaporate the solution. *Manganese brown*, or *bronze*, is produced by immersing the fabric in a solution of sulphate of manganese, and then in one of dilute caustic alkali to precipitate the protoxide, which is raised to a higher state of oxidation either by simple exposure to the air, or, more rapidly, by transmitting it through a solution of bleaching powder.

Processes for the Recovery of Manganese.—It has been customary for manufacturers who eliminate chlorine on the large scale, to throw away the chloride of manganese that results. To prevent this enormous loss of valuable material, various methods have been proposed and patented for recovering the manganese, or reconverting the chloride into the binoxide or sesquioxide. It is well known that the protoxide of manganese is readily converted by the oxygen of the air into the sesquioxide by gentle ustulation; and it was mentioned long ago by Forchhammer, that carbonate of manganese, when heated in an open vessel to 500° F. (260° C.), is converted for the most part into binoxide, an observation which does not seem, until lately, to have attracted that degree of attention which its importance merits. The principal processes for the recovery of manganese, at present in use, are those of Dunlop and Weldon, for which see article on Chlorine.

Colours.—Various colours can be obtained directly or indirectly from the natural manganese or a recovered oxide. A brown colour, according to T. Rowan, can be got by heating the recovered oxide, or by freely exposing it to the air; a green colour, by heating the carbonate of manganese in a closed vessel, with a tube loosely filled with carbon to allow gases to escape, but prevent access of air. By cautiously heating the carbonate of manganese with free access of air a black pigment is obtained. A pure violet colour, according to Leikauf, can be obtained by fusing recovered oxide of manganese with phosphoric acid, boiling the fused mass with ammonia or carbonate of ammonia, filtering the oxide of manganese which separates, and evaporating the filtrate to dryness. The dried residue is then fused, and when cool boiled with water. The insoluble forms a violet powder, known as Manganese or Nürnberg Violet. The addition of a salt of iron to the first fusion produces a blue shade. In addition to these pigments there is a green colour, consisting essentially of manganate of barium, which Rosenstiehl obtains by heating a moist mixture of from 3 to 4 parts baryta, 2 parts nitrate of baryta, and ·5 part oxide of manganese. On heating with water an insoluble crystalline powder of a pure green colour is obtained.

Quantitative Estimation.—Manganese is weighed almost invariably as the red oxide, Mn_3O_4, 229 parts of which are equivalent to 165 of metallic manganese, 213 of protoxide, and 261 of binoxide. When no other base is present, or only the alkalies, the moderately dilute solution is heated to boiling, and the manganese is thrown down as carbonate by the addition of carbonate of soda in excess. The precipitate is collected on a filter, washed with boiling water, dried and ignited over a powerful lamp or in a furnace, until the weight ceases to vary. The residue in the crucible is pure red oxide. If the liquid contains ammoniacal salts, it must be boiled with

carbonate of soda in excess until the odour of the volatile alkali is no longer perceptible.

When any of the metals precipitable by sulphide of hydrogen are contained in the liquid, it must be rendered acid by the addition of hydrochloric acid, and treated with this agent, in order to remove them. Sesquioxide of iron is most readily separated by the addition of succinate of ammonia to the nearly neutral liquid. Manganese may be separated from the alkalies, earths, and the oxides of iron, nickel, and zinc, by the ingenious method of SCHIEL. The acid menstruum is nearly neutralized with carbonate of soda, acetate of soda added, and chlorine gas passed through the liquid to saturation. The manganese is completely deposited as hydrated binoxide, which may be converted into red oxide by ignition; the other bases remain in solution. The absolute separation of manganese and cobalt is attended with considerable difficulty; but the following simple method gives results which are sufficiently accurate for all technical purposes:—The two metals are precipitated by sulphide of ammonium and excess of acetic acid then added, when the sulphide of manganese dissolves, and the sulphide of cobalt remains intact.

The separation of manganese from nickel is given under the latter metal. Having obtained the sulphide of manganese by the process mixed with sulphide of zinc, it will be well to give here the mode of obtaining the manganese *per se*. Dissolve the sulphide in hydrochloric acid, then nearly neutralize with carbonate of soda, add acetate of soda, and next conduct chlorine gas into the mixture. The manganese salt is thereby decomposed, and the whole of the manganese separates as binoxide. The zinc remains in solution.

For the valuation and testing of manganese ores, the reader is referred to Bleaching Powder under the article CHLORINE.

Physiological Effects.—The effects of manganese upon the system are imperfectly known. KAPP regards it as a permanent stimulant, and says it promotes the appetite and digestion. VOGT places it among the tonics, and considers it to be intermediate between iron and lead; but his views are altogether theoretical, as he does not seem to have prescribed it. Dr. COUPER has described several cases of disease which took place among the men engaged in grinding it at the chemical works of Messrs. TENNANT & Co. in Glasgow; from these it appears that, when slowly introduced into the system, it produces paralysis of the motor nerves. The disease commences with symptoms of paraplegia. It differs from the paralysis of lead in not causing *colica pectorum*, or constipation; and from mercury, in first affecting the lower extremities, and in not exciting tumours of the afflicted part.

Manganese is rarely used in medicine; it appears to have been employed in the last century in the treatment of inflammatory fevers. GRILLE long since observed that the workmen in the manganese mines at Maçon were not subject to the itch; and that others who became affected with this disease were cured by working in the mines. This led him, as well as MORELOT and others, to employ it in cutaneous maladies. KAPP administered it, as well as the salts of manganese, both internally and externally in various forms of syphilis; he used it with benefit in herpes, scabies, and the scorbutic diathesis. BRERA gave it in chlorosis, scorbutus, hypochondriasis, hysteria, &c. OTTO administered it in cachectic complaints, with favourable results. ODIER employed it in cardialgia. It has been applied as an absorbent in the treatment of old ulcers, as a depilatory, and as a remedy for skin diseases, especially itch and porrigo. KUGLER gave it with benefit in scrofula.

HUNEFELD gave to a rabbit nearly 2 drachms of manganic acid in three days, in doses of 10 or 15 grains. The only obvious effect was increased secretion of urine. The animal being killed, the peritoneum and external coat of the colon were found of a greenish colour (protoxide of manganese is of a pale grass-green colour), the muscles were readily lacerated and livid, the liver was inflamed, the bile increased.

MANURE.—By manure we understand all substances which are applied to land for the purpose of increasing the amount of plant-food which it contains. To understand the science of manuring in its application to English agriculture, we must be acquainted, in the first place, with the food requirements of our crops, and the manner in which these requirements are met in nature.

The constituents of a plant fall under three great divisions. First, there is water, which forms by far the larger part of all growing plants. The dry matter may next be divided into combustible carbonaceous matter, and into incombustible matter or ash. The combustible ingredients include the vegetable fibre, sugar, starch, fat, albuminoids, the colouring and flavouring principles, &c. These are very commonly called organic substances, while the ingredients of the ash are termed inorganic. This distinction is, however, not an accurate one, as the constituents of the ash, so long as they form a part of the plant, have as much right to be called organic as albumin or cellulose, being equally indispensable parts of the vegetable structure.

To illustrate the composition of a crop, we will take as an instance a crop of meadow hay, weighing when mown 5 tons, and yielding $1\frac{1}{2}$ ton of hay when made. Its constituents, expressed in pounds, will be about as follows:—

TABLE I.—COMPOSITION OF MEADOW HAY.

Water,			8378
Carbon,	1315	Combustible matter,	2613
Hydrogen,	144		
Nitrogen,	49		
Oxygen and sulphur,	1105		
Potash,	56·3	Ash,	209
Soda,	11·9		
Lime,	28·1		
Magnesia,	10·1		
Oxide of iron,	·9		
Phosphoric acid,	12·7		
Sulphuric acid,	10·8		
Chlorine,	16·2		
Silica,	57·5		
Sand, &c,	4·5		
Total crop,			11,200 lbs.

Of these ingredients, the water will have been derived from the soil through the roots. It seems doubtful whether the leaves of plants have any power of imbibing water.

The carbon will have been obtained almost wholly from the atmosphere through the agency of the leaves. The air at the surface of the earth contains in 10,000 volumes about $3\frac{1}{2}$ volumes of carbonic acid gas, or 1 lb. of carbon in 3500 cubic yards of air of the ordinary temperature and pressure. The carbonic acid is absorbed through the cuticle of the plant, which is more pervious to this gas than to the nitrogen and oxygen which form the main bulk of the atmosphere, and is decomposed under the influence of light, oxygen being evolved, and the carbon retained by the plant. This fixation of carbon from the atmosphere under the influence of light, is a function exercised more or less by all the green parts of a plant, but especially by the leaves. It seems possible that plants may obtain a small part of their carbonic acid in solution through the roots; but the fact that wheat crops containing a ton of carbon have been grown annually at Rothamsted on the same land for twenty-five years, without any artificial supply of carbon to the soil, proves that in this case, at least, the atmosphere is an amply sufficient source of nutriment.

The nitrogen in the crop will have been obtained almost entirely from the soil. The amount of ammonia gas in the atmosphere is very small; according to Schloesing, it varies from about 1 lb. in 6,000,000 cubic yards, to 1 lb. in 119,000,000 cubic yards. The experiments of Sachs, Meyer, and Schloesing have proved that plants are capable of taking up nitrogen from an atmosphere artificially enriched with ammonia, but even then not apparently to the extent required for healthy vigorous growth. Boussingault has distinctly shown that the ordinary atmosphere is quite incapable of supplying sufficient nitrogen for the requirements of a plant. This fact leads to the further conclusion established by the investigations of Boussingault, and of Lawes, Gilbert, and Pugh, that plants are incapable of assimilating the free nitrogen of the air. But although crops obtain directly from the atmosphere a very small quantity of the nitrogen which they contain, yet indirectly the amount of nitrogen derived from the atmosphere is undoubtedly considerable. The quantity of ammonia and nitric acid annually conveyed to the soil by rain, and the ammonia directly absorbed from the atmosphere by the soil itself, are both, under certain circumstances, very important. The form of nitrogen most suitable for the assimilation of plants is nitric acid; ammonia, urea, uric and hippuric acids, are also available forms of nitrogen.

The hydrogen and oxygen, which form a part of the combustible constituents of a plant, will be obtained as water from the soil. The sulphur will also be taken from the soil in the form of sulphuric acid.

The whole of the ingredients of the ash will be obtained from the soil.

To sum up the above facts, we may say that a crop derives nearly all its carbon directly from the atmosphere through the agency of its leaves; but that, with the exception of a small quantity of nitrogen taken up as gaseous ammonia, the whole of the other ingredients of a crop are obtained from the soil through the roots.

Let us now imagine that the crop of grass just described is the produce of a natural meadow. If the grass is not cut for hay, nor consumed by animals, but is allowed to grow in a wild state without check, it is obvious, in the first place, that the soil can suffer no loss of the incombustible elements of the crop. In autumn a great part of the grass produced in summer would decay; but as decay is merely a more or less complete combustion, it would have no influence on the incombustible constituents, and with the decay of the grass these would be returned to the soil. During the death of the crop there would be a great loss of water, a considerable loss of carbon, and some loss of nitrogen. At the end of the year the nett result of the vegetable growth, and of the atmospheric influences during this period, would be that the amount of incombustible constituents in the field would remain unchanged, while the amount of carbon and nitrogen in the soil would be increased. A continual course of vegetation under these circumstances would lead to the accumulation on the surface of the field of a large quantity of vegetable soil, rich in carbon, and containing also a notable amount of nitrogen.

Let us next assume that the produce of the meadow, instead of being left to decay, is consumed by animals. If the animals are wild, and their bodies are naturally returned to the soil at death, we shall here again have no loss of the ash constituents of the crop. The loss of nitrogen will probably also be little greater than that which took place in the previous instance during the decay of the grass. Experiments have failed to establish that nitrogen is lost in the animal economy; the loss would therefore be confined to that resulting from the exposure of the voidings to the atmosphere, and to the gases evolved during the decomposition of the body at death. The main effect of the consumption of the grass as animal food would be the speedy combustion of the carbon, which would be returned to the atmosphere as carbonic acid. There would thus in this case be far less accumulation of vegetable soil on the land; and it is probable that, as a consequence of this, there would also be but little accumulation of nitrogen. Nitrogenous peaty matter is very permanent, and may accumulate to any extent; but animal nitrogenous matter is easily converted into nitrates, which are very soluble, and readily pass into the drainage water during heavy rain.

Turning from these simple natural conditions of pasture to the conditions of pasture in ordinary agriculture, we observe at once that one of the characteristic features of agricultural operations is the removal of more or less of the produce from the soil. If the grass is cut for hay, it is plain that the whole of the constituents of the crop are taken from the land. If the pasture is fed by stock, which are afterwards sold, it is evident that the soil is deprived

of the cinereal matter which has formed the bone, and which is contained in the blood and flesh of the animal. A quantity of nitrogen and carbon will also be removed in the animal body. Sales of wool and milk, in the same way, represent matter taken out of the soil. In ordinary agriculture we have then a necessity for artificial manuring; we must bring back on to the land important constituents taken from it, if its fertility is to be permanently maintained.

The produce, whether vegetable or animal, which a farmer removes from his fields is clearly not absolutely lost. It is consumed by man or by other animals; and could this consumption take place on the farm, and the excreta resulting from the food so consumed be returned to the fields which yielded the produce, the manure required to maintain the fertility of the land would be at once obtained. This simple and perfect form of agriculture can be carried out to only a limited extent. The produce of the farmer's land is in most cases consumed in towns at a distance from the farm, and no method has yet been contrived for converting the excreta of a population into a portable manure which could be returned with economy to the land which supplied the food. In villages much might be done by the careful use of the earth-closet system; but in large towns the sewage system is apparently indispensable; and under this system a complete return of the manure to the land is hopeless. All efforts have failed to precipitate from sewage more than a small fraction of its valuable constituents. By employing sewage in irrigation, a large proportion of its nitrogen and other constituents may indeed be recovered, and made to serve as food for crops; but the benefit of this manuring must clearly be confined to the land in the neighbourhood of towns. However great, therefore, may be the advantages to be derived from sewage irrigation, it can never solve the problem of returning to the land the elements of fertility removed in the crops.

We will now consider what quantities of the more important elements of plant food are removed from the soil by the various crops on a farm. The following table gives the weight of average crops of wheat, barley, oats, meadow hay, clover hay, beans, turnips, swedes, mangels, and potatoes; and also their composition, as far as this is necessary for our present purpose. The "total ash" represents ash deprived of its carbonic acid; its quantity therefore corresponds with the amount derived from the soil.

TABLE II.—THE WEIGHT AND COMPOSITION OF ORDINARY FARM CROPS.

	Weight of Crop.		Total Ash.	Nitrogen.	Sulphur.	Potash.	Soda.	Lime.	Magnesia.	Phosphoric Acid.	Chlorine.	Silica.
	At Harvest.	Dry.										
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Wheat, grain, 30 bushels, ...	1,800	1,530	31	33	2·7	9·7	·9	1·0	3·7	14·3	·2	·5
" straw, ...	3,158	2,653	158	12	5·1	18·2	2·5	9·2	4·0	8·4	1·7	110·6
Total crop, ...	4,958	4,183	189	45	7·8	27·9	3·4	10·2	7·7	22·7	1·9	111·1
Barley, grain, 40 bushels, ...	2,080	1,747	46	34	2·9	10·1	1·3	1·2	3·8	15·1	·5	12·5
" straw, ...	2,447	2,080	110	12	3·2	23·7	4·5	8·5	2·6	4·9	2·8	59·5
Total crop, ...	4,527	3,827	156	46	6·1	33·8	5·8	9·7	6·4	20·0	3·3	72·0
Oats, grain, 45 bushels, ...	1,890	1,625	54	38	3·2	8·5	1·4	2·0	3·9	11·8	—	24·8
" straw, ...	2,835	2,353	140	14	4·8	29·6	5·9	9·8	5·3	7·1	5·5	69·3
Total crop, ...	4,725	3,978	194	52	8·0	38·1	7·3	11·8	9·2	18·9	5·5	94·1
Meadow hay, 1½ ton, ...	3,360	2,822	208	49	5·7	56·3	11·9	28·1	10·1	12·7	16·2	57·5
Clover hay, 2 tons, ...	4,480	3,763	255	102	9·4	87·4	4·1	86·1	30·9	25·1	9·4	6·8
Beans, grain, 30 bushels, ...	1,920	1,613	57	77	4·4	23·0	·8	2·9	3·8	22·3	1·5	·8
" straw, ...	2,240	1,848	130	22	4·9	58·1	4·9	30·2	10·3	9·2	18·1	6·9
Total crop, ...	4,160	3,461	187	99	9·3	81·1	5·7	33·1	14·1	31·5	19·6	7·7
Turnips, root, 17 tons.....	38,080	3,126	218	71	15·2	108·6	17·0	25·5	5·7	22·4	10·9	2·6
" leaf, ...	11,424	1,531	146	49	5·7	40·2	7·5	48·5	3·8	10·7	11·2	5·1
Total crop, ...	49,504	4,657	364	120	20·9	148·8	24·5	74·0	9·5	33·1	22·1	7·7
Swedes, root, 14 tons	31,360	3,349	163	74	14·6	63·3	22·8	19·7	6·8	16·9	6·8	3·1
" leaf, ...	4,704	706	75	28	3·2	16·4	9·2	22·7	2·4	4·8	8·3	3·6
Total crop.....	36,064	4,055	238	102	17·8*	79·7	32·0	42·4	9·2	21·7	15·1	6·7
Mangels, root, 22 tons,.....	49,280	5,628	410	96	4·9	191·1	75·4	24·2	19·7	34·0	40·6	16·4
" leaf, ...	18,233	1,654	280	51	9·1	71·4	65·2	29·1	27·2	15·1	49·8	9·2
Total crop, ...	67,513	7,282	690	147	14·0	262·5	140·6	53·3	46·9	49·1	90·4	25·6
Potatoes, tuber, 6 tons, ...	13,440	3,360	126	47	2·7	75·4	2·0	2·9	5·7	24·1	3·5	2·9
" haulm,*.....	4,274	954	50	20	2·1	1·1	2·0	22·7	12·4	2·7	1·9	2·1
Total crop, ...	17,714	4,314	176	67	4·8	76·5	4·0	25·6	18·1	26·8	5·4	5·0

* Calculated from a single analysis only.

It is interesting to observe that the quantity of dry matter contained in average crops is generally very similar; and if we except mangel wurzel (which is never grown unless highly manured), and meadow hay, the single crop of which does not represent the whole year's produce, the uniformity is very great, being about 4000 lbs. per English acre. The bulk of the dry matter, we have already seen, is derived from the atmosphere, through the agency of sunlight on the plant. It would appear from the above facts that very different plants, when placed under equally favourable circumstances, and covering the same area of ground, will assimilate in their annual growth very similar amounts of carbon.

The other important combustible ingredient of crops, nitrogen, is seen to occur in very various proportions. Roughly speaking, the graminaceous crops—wheat, barley, oats, and meadow grass—all contain 50 lbs. of nitrogen; while the leguminous crops—clover and beans—and the various root crops (potatoes excepted), all contain at least twice this amount of nitrogen. The same comparison holds good whether we exclude or include the straw and leaf—bean corn containing twice as much nitrogen as cereal corn, and a crop of turnip roots deprived of leaf containing twice as much nitrogen as the grain of wheat or barley. It is evident, therefore, that the sale of one class of crops will deprive the farm of far more nitrogen than the sale of the opposite class.

In the quantity of sulphur required, the turnip crop stands at the head of all the others.

It will be unnecessary to pass in review the whole of the ash constituents mentioned in the table. It is doubtful whether soda is essential to the perfect growth of plants; it is frequently entirely absent in potatoes, parsnips, and in cereal grains, though always present in beet. Chlorine and silica may also be omitted from notice. Cereals may, according to the German experimenters, be brought to considerable perfection without either of these substances being supplied; it is probable, however, that both are of some use in the chemical operations within the plant, though not required to build up tissue. Buckwheat grown without chlorine is speedily affected by "starch-sickness;" and Lawes and Gilbert have found silicates to increase the produce of a meadow which had been deprived of silica by continuous cropping.

Very small quantities of lime and magnesia are required by the cereal crops; the lime is chiefly found in the straw. In meadow hay lime is much more abundant; grass in its composition, indeed, greatly resembles a crop of unripe straw. In root crops lime is still more abundant, preponderating in the leaf; it is also very abundant in bean straw. It reaches its highest amount in clover hay. In both clover and bean straw lime is a very variable constituent; on soils rich in potash these crops contain comparatively little lime, while on calcareous soils poor in potash the amount of lime taken up is very large. Magnesia is most abundant in clover and in mangel wurzel.

The most important of the ash constituents of a crop, agriculturally speaking, are undoubtedly phosphoric acid and potash; these are not only absolutely necessary for the formation of vegetable tissue, but also generally present in the soil to only a small extent. Phosphoric acid is chiefly concentrated in the seed of the plant; in the case of a biennial plant, as the turnip, &c., it is also found stored up in the root at the end of the first season's growth. Potash is usually present in much greater quantity than phosphoric acid. It occurs more abundantly in the straw of cereal crops than in the grain. In hay it reaches a large amount. The maximum contents is, however, reached in the root crops; here potash, like phosphoric acid, is stored up in the root at the end of the first period of growth.

The facts and figures now before us will suffice to point out the nature and extent of the exhaustion which takes place when crops are entirely removed from the land. In practice, however, as is well known, the farmer usually consumes upon the farm the whole of his straw, hay, and roots, and sells only corn, meat, wool, and milk. Where this is strictly done the loss of cincreal matter is very small. The following table shows approximately the loss in lbs. per acre of the three most important constituents of crops during an ordinary four-course rotation, in which only corn and meat are sold:—

TABLE III.—LOSSES PER ACRE DURING A FOUR-COURSE ROTATION.

	Nitrogen.	Potash.	Phosphoric Acid.
	Lbs.	Lbs.	Lbs.
By feeding swedes (14 tons).....	11·1	·24	1·80
By sale of barley (40 bushels)...	34·0	10·10	15·10
By feeding seeds* (3 tons of hay).....	18·7	·40	3·20
By sale of wheat (30 bushels), ..	33·0	9·70	14·30
By feeding straw (½ ton), ...	·7	·02	·12
Total loss in four years,..	97·5	20·46	34·61
Average loss each year,.	24·4	5·11	8·65

* Assumed as half clover, half grass.

It appears from these figures that the annual loss of phosphoric acid per acre would be about 8½ lbs., and the loss of potash 5 lbs. The amount of nitrogen removed from the land is far more considerable; it cannot, however, be stated with much exactness. It is assumed in the table that 15 per cent. of the nitrogen of the swedes, hay, and straw are either retained by the animal, or unavoidably lost during the formation of the manure; this is the provisional assumption of Messrs. Lawes and Gilbert.

On a farm in which there are a variety of exports and imports, it will be necessary to state each item separately, and to balance the totals against each other, if the losses or gains are to be ascertained with any exactness. Table II. has shown the composition of the vegetable exports of a farm, the following table will give the necessary information relating to the animal exports:—

TABLE IV.—COMPOSITION OF THE ANIMAL EXPORTS OF A FARM.

	Nitrogen.	Phosphoric Acid.	Potash.	Lime.	Magnesia.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
Fat ox, 1000 lbs. fatted live weight,	23·18	16·52	1·84	19·20	·63
Fat sheep, " "	19·60	11·29	1·59	12·80	·50
Fat pig, " "	17·57	6·92	1·48	6·67	·35
Wool, unwashed, 1000 lbs.	73·00	1·00	40·00	1·00	·70
Milk, 1000 lbs.	5·50	2·00	1·70	1·60	·20
Cheese, 1000 lbs.	44·00	11·50	2·50	6·90	·30

The composition of fat stock given in this table is deduced from the experiments at Rothamsted, in which the entire bodies of animals were submitted to analysis. The amount of potash contained in unwashed wool has been frequently determined by French and German chemists; their results show nearly 5 per cent. to be present. As, however, the fleeces were in many cases those of merino sheep, which are carefully protected from rain, it is probable that the ordinary English fleece will contain less. The ash constituents of cheese are deduced from two German analyses, the only ones the writer is acquainted with.

The data now before us afford pretty full information as to the loss of cinereal matter which a farm may suffer, either by sale of crops or by sale of animal produce. A further loss of the ash constituents of plants will take place in the drainage water from the fields. Owing, however, to the wonderful power of retaining phosphoric acid and potash possessed by fertile soil, the losses of these important elements will be very small, and in the case of the former of them practically *nil*. Large quantities of lime and soda, and of sulphuric acid and chlorine, will, however, be lost during winter drainage.

The information supplied as to the loss of nitrogen is less complete; the nitrogen lost to the farm will indeed be always greater than the nitrogen sold. The extra loss occurs partly during the making of the manure: this loss does not admit of general estimation, but will be greater or less according to the management pursued. There will further be an important loss of nitrogen in the drainage water. Ammonia is retained by soil with great persistence; the nitrogenous organic matter of soils is also tolerably insoluble. Nitrates, on the other hand, are retained by soil to only a small extent, and being very soluble, are easily washed out by rain. As ammonia is rapidly oxidised into nitric acid in a porous soil, and nitrogenous organic matter suffers more slowly a similar change, very considerable losses of nitrogen may take place during winter drainage. In the case of soils deficient in porosity, or from other causes ill supplied with oxygen, little or no loss of nitric acid will take place; but it seems probable from Schloesing's experiments, that under these circumstances the decomposition of the nitrogenous matter will yield free nitrogen, which will be equally lost to the soil.

We pass now to the imports of a farm, and will consider first the natural and very important import —rain.

Rain contains nitrogen in the form of ammonia, and in the form of nitric and nitrous acid. The ammonia present is merely dissolved atmospheric ammonia, and the rain simply returns to the earth ammonia previously volatilized from the earth's surface. Ammonia is, according to Schloesing, principally volatilized from the ocean in tropical latitudes; from thence it is carried by the diffusion of gases and atmospheric currents to every part of the globe. The nitrates lost to the soil by drainage finally reach the sea; here they feed marine plants, which in their turn sustain marine animals; the plants and animals in their decay furnish ammonia, which, diffusing into the atmosphere, is carried over continents, and becomes once more food for terrestrial vegetation. The nitrous and nitric acid of rain are not derived from the earth, but are actually generated in the atmosphere, electric discharges having the power of causing the free nitrogen and oxygen of the air to combine. The quantity of combined nitrogen thus generated is, however, but small; and rain always contains more nitrogen in the form of ammonia than in the form of nitric or nitrous acid. The amount of nitrogen brought down in the annual rain-fall has been many times determined; it apparently varies very much. The average of seventeen series of experiments, made chiefly in Germany, in each of which the rain-fall was examined for a whole year, gives 9·45 lbs. of nitrogen as the amount annually contributed to an English acre. The average rain-fall in these experiments was about 22¼ inches. A two years' determination at Rothamsted gave 7·47 lbs. as the annual supply of nitrogen by rain. Besides nitrogen, rain supplies small quantities of chloride of sodium, and other salts. The rain at Valencia, on the west coast of Ireland, would supply, according to Dr. A. Smith's analysis, 17½ lbs. of common salt per acre for each inch of rain that fell. In inland country places of England and Scotland the amount of chloride of sodium would, according to the same authority, not on an average exceed 1½ lb. per inch of rain. At Cirencester, 35 miles from the Bristol Channel, Professor Church finds the chlorine in the annual rain-fall equivalent to 30 lbs. of common salt per acre, and in exceptional years this is much increased. In the neighbourhood of towns, sulphuric acid and other impurities are contained in rain water.

It is probable that besides the amount of nitrogen brought to the soil by rain, there is, in some way not well understood, a further considerable amount of nitrogen derived from the atmosphere, either by the growing crops or by the soil itself. It was long ago observed by Boussingault that the nitrogen

contained in crops moderately manured does in the long run exceed the nitrogen supplied in the manure, and that to a greater extent than can be accounted for by the agency of rain. The field experiments at Rothamsted afford the best evidence on this point. Wheat and barley crops grown year after year on the same land, manured with phosphates, potash, and other ash constituents, but receiving no nitrogen, have yielded on an average 18 to 22 lbs. of nitrogen annually as corn and straw, during twenty-four years. These crops are, however, slowly falling off; it is probable, therefore, that a part of the nitrogen has been obtained from former accumulations in the soil. Beans grown with purely cinereal manures have yielded in twenty-one crops an average of 45 lbs. of nitrogen per annum; this crop, too, has fallen off. The strongest evidence of assimilation of nitrogen from the atmosphere is, however, to be found in the experiments with meadow land, and with a rotation. With meadow land, manured with purely cinereal manures, the average nitrogen in the produce during twenty years has reached the large amount of 55 lbs. On this plot there is at present no sign of falling off in the produce. The cinereal manure has developed a large amount of clover, and this is doubtless one reason of the nitrogenous character of the crop. On the rotation field, whether we take the entirely unmanured rotation, or the rotation receiving superphosphate only, or that which is liberally manured both with nitrogen and ash constituents, we find in each case that the average annual yield of nitrogen by the crops during twenty-eight years is more than 36 lbs. in excess of that supplied as manure. In the case of the liberally manured rotation, a falling off in the crops is hardly to be expected.

A part of the atmospheric nitrogen thus assimilated is doubtless taken up by the crop as gaseous ammonia from the atmosphere. The soil will also absorb some ammonia from the air; but it seems doubtful whether these actions can fully account for the considerable assimilation of nitrogen which appears in the above experiments—an assimilation which seems specially associated with leguminous crops. P. Déhérain believes that the humus of soils is capable, in the absence of oxygen, of combining with the free nitrogen of the air, which he supposes, under these circumstances, to be first converted into ammonia. This enrichment of the soil with nitrogen he believes takes place in the lower layers of the soil. The reaction in question is very far from being established. Berthelot has recently made experiments, from which he concludes that plants can assimilate free nitrogen when exposed to certain electrical influences. This action, also, requires to be substantiated.

It is clear from what has now been said, that it is not only difficult, but impossible to express with exactness many of the gains and losses of nitrogen upon a farm.

We turn next to the artificial imports to a farm.

Manure from Feeding Stuffs.—A large class of the imports to a farm consists of the various foods purchased for the stock, and the manure from which is eventually applied to the land. The following table gives the average composition in 1000 parts of the more common feeding stuffs employed on a farm, so far as their manurial value is concerned:—

TABLE V.—COMPOSITION OF ORDINARY FEEDING STUFFS IN 1000 PARTS.

	Dry Matter.	Nitrogen.	Potash.	Phosphoric acid
Cotton cake (decorticated),	900	66·0	15·0 ?	31·2
Rape cake,	900	48·0	13·2	24·6
Linseed cake,	885	45·0	14·7	19·6
Cotton cake (undecorticated)	885	37·0	20·1	22·9
Linseed,	905	36·0	12·3	15·4
Palm-kernel meal (English),	930	25·0	5·5	12·2
Beans,	850	40·0	12·0	11·6
Peas,	860	36·0	9·8	8·8
Malt dust,	905	38·0	19·5	17·2
Bran,	865	22·0	14·8	32·3
Oats,	860	20·0	4·5	6·2
Wheat,	850	18·0	5·4	8·0
Barley,	840	16·5	4·9	7·3
Maize,	880	16·0	3·6	6·1
Clover hay,	840	23·0	19·5	5·6
Meadow hay,	840	14·6	16·8	5·8
Bean straw,	825	10·0	25·9	4·1
Wheat straw,	840	4·0	5·8	2·6
Barley straw,	850	5·0	9·7	2·0
Oat straw,	830	5·0	10·4	2·5
Potatoes,	250	3·5	5·6	1·8
Mangels,	115	2·0	3·9	·7
Swedes,	107	2·3	2·0	·6
Carrots,	142	1·6	3·2	1·0
Turnips,	82	1·9	2·9	·6

The value of any food, regarded as a source of manure, will depend on the proportion of nitrogen, phosphoric acid, and potash which it contains, and chiefly on the first-named constituent. The table just given shows that of all foods oil-cakes contain most nitrogen; they are also rich in phosphoric acid and potash. Leguminous seeds, as beans and peas, are also very rich in nitrogen. The cereal grains are much poorer both in nitrogen and ash constituents than the two classes of foods just named; certain products, however, as malt-dust and bran, have a much higher manurial value. Clover hay is richer in nitrogen than the cereal grains, but grass hay stands below them. Hay always contains an abundance of potash. Roots contain about the same proportion of nitrogen in their dry matter as the cereal grains, but a much larger proportion of potash. Straw has the lowest manurial value of any of the foods named; bean straw stands highest.

When food is consumed by an adult animal whose weight remains constantly unchanged, the total quantity of nitrogen and of ash constituents found in the liquid and solid excrements will be the same as that in the food consumed. A part of the albumin, phosphates, &c., of the food will, indeed, be stored up, being used in the production of new tissue; but the quantity thus assimilated will merely supply the place of a corresponding waste, the weight of the animal remaining constant. With a working horse or ox the farmer will obtain in the

manure, practically, the whole of the nitrogen and ash constituents which were originally present in the food. If, however, an animal is increasing in weight, is breeding, or is yielding to the farmer wool or milk, it is evident that a part of the food is finally converted into animal increase, and that the whole of the nitrogen and ash constituents of the food will not be found in the manure. The value of the manure will thus depend, not only on the composition of the food, but also, to a less extent, on the condition of the animal which consumes it.

Lawes has shown by experiment that something less than 5 per cent. of the nitrogen contained in the mixed diet (cake, chaff, and roots) of a fattening ox or sheep is retained by the animal, and that the proportion retained by pigs fed on barley meal is about 14 per cent. These figures do not include the loss of nitrogen which may take place during the collection or preservation of the manure. The composition of the bodies of oxen, sheep, and pigs further teach us that for 100 of nitrogen stored up in the animal there will be retained the following proportions of phosphoric acid and potash:—

	Phosphoric Acid.	Potash.
Oxen,	71	8
Sheep,	58	8
Pigs,	39	8½

The proportion of phosphoric acid assimilated will, however, be greater than appears from these figures in the youth of the animal, and less during the final period of fattening.

On the very important question, whether the nitrogen of animal excrements is as efficacious as a manure for crops as the nitrogen of such artificial manures as nitrate of sodium and ammonium salts, exact information is at present wanting; experiments on this point are now in progress on the Duke of Bedford's estate at Woburn.

Farm-yard Manure.—This staple manure of every farm consists of the excrements of animals, distributed through a large bulk of litter employed as an absorbent. It is important for the farmer to remember that the larger part of the nitrogen voided by animals is in the form of urine, and that consequently great care must be taken for the preservation of the liquid ingredients of the manure. With cattle and sheep fed on ordinary diets, 60 to 80 per cent. of the nitrogen leaving the animal will be found in the urine; the richer the diet is the greater will be the proportion of nitrogen excreted in the liquid form.

Farm-yard manure contains all the necessary ingredients of plant food, and is for this reason a perfect manure, possessing in itself all that is required to restore fertility to exhausted land. In this respect it differs widely from most artificial manures, which usually supply but one or two of the individual ingredients of plant food, and require therefore to be applied with judgment to yield an economic result.

The composition of farm-yard manure will vary greatly, according to the nature of the food and litter, the character of the stock, the extent to which the manure has rotted, and the care and skill which has been bestowed on its management. The following is given by Professor Wolff as the average composition of 100 parts of farm-yard manure:—

TABLE VI.—PERCENTAGE COMPOSITION OF FARM-YARD MANURE.

	Fresh.	Moderately Rotten.	Thoroughly Rotten.
Water,	71·0	75·0	79·0
Organic matter,	24·6	19·2	14·5
Ash,	4·4	5·8	6·5
Potash,	·52	·63	·50
Soda,	·15	·19	·13
Lime,	·57	·70	·88
Magnesia,	·14	·18	·18
Phosphoric acid,	·21	·26	·30
Sulphuric acid,	·12	·16	·13
Chlorine,	·15	·19	·16
Silica,	1·25	1·68	1·70
Nitrogen,	·45	·50	·58

The above represents the composition of yard manure of rather poor quality. With animals receiving a moderate amount of cake, ·60 of nitrogen and ·30 of phosphoric acid would be found in good fresh dung.

The analyses in the table show the alteration which dung suffers during fermentation. The organic matter gradually disappears, being converted into water and carbonic acid, while the ash constituents and water increase. Well-fermented dung is a more concentrated manure than fresh dung, as it has lost considerably in bulk without any important waste of nitrogen or ash constituents. If, however, the fermenting dung has been exposed to rain, and has suffered loss from drainage, the diminution of nitrogen and of soluble ash constituents will be very considerable. There is no doubt that in practice a large amount of most valuable manurial matter is lost by the unrecovered drainage from farm yards and from manure heaps.

The immediate effect of farm-yard manure is, under most circumstances, much less than that of an artificial manure supplying the same amount of plant food. Farm-yard manure supplying 100 lbs. of nitrogen will produce a much less effect on a corn or grass crop than a dressing of guano, ammonium salts, or nitrate of sodium, supplying the same quantity of nitrogen. This is owing to the slow decomposition of the organic matter contained in the yard manure. This decomposition is probably slower the more litter has been used. A part of the nitrogen of the yard manure not recovered in the first crop is appropriated by following crops, but it is doubtful whether the final return ever equals that from artificial manures judiciously applied.

Sea-weed is largely used as a manure in many places bordering on the sea. It differs much in composition, according to the kind of weed collected, the season of the year, and the extent to which it is mixed with sand, or covered with shells and marine animals. An analysis of Anderson's of the mixed weeds collected on the Orkney islands will give a general idea of the composition of this manure—

Water,	80·44
Organic matter,	9 25
Ash,	10·31
	100·00
Nitrogen,	·45
Potash,	1 95
Phosphoric acid,	·47

DAVY found in dry sea-weed from 1·58 to 4·65 per cent. of nitrogen. The usual amount seems to be 1·5 to 2 per cent. STANFORD found in various dry weeds 2·04 to 8·96 per cent. of potash. The average of fifteen analyses by different chemists of species of *Fucus* and *Laminaria* is 3·18 per cent of potash; the latter species is much richer in potash than the former. The phosphoric acid in the ash of sea-weed is always small in quantity. The ash is very rich in sulphates. Fresh sea-weed is, on the whole, very similar to farm-yard manure in its contents in nitrogen and potash, but unless associated with animal organisms is deficient in phosphoric acid.

Guano.—This manure was introduced into England in 1839, and for the last thirty years it has held the first place among our artificial manures. During this period about 200,000 tons have been annually consumed in the United Kingdom. Guano is, however, fast becoming a subject for bygone history; the best and largest deposits are exhausted, and probably a few more years will see the end of the remainder.

Guano is formed of the excrements and carcasses of sea fowl, accumulated for the most part during untold centuries. The fresh excrements are highly nitrogenous, and consist chiefly of uric acid and phosphates. If the climate is hot and dry the deposits are quickly dessicated, and suffer only a moderate amount of decomposition from heavy dews and sea spray; the result in this case is a nitrogenous guano, such as is found on the Peruvian coast. But if the climate is such that the guano is exposed to rain, a great loss of nitrogenous matter takes place, partly by solution and drainage, but still more by conversion into carbonate of ammonium, which volatilizes; the residual guano will in this case consist chiefly of insoluble phosphates. The coast of Peru, between latitude 14° and 21° S., is almost the only spot where the conditions of climate allow the preservation of a nitrogenous guano; the guano from other localities is mainly phosphatic, unless of very recent origin, and removed before much decomposition has taken place.

The following table shows the general composition of the principal guanos:—

TABLE VII.—AVERAGE PERCENTAGE COMPOSITION OF GUANOS.

	Peruvian.										African.				Pacific Ocean.	
	Angamos.	Chincha.	Ballestas.	Guanape.	Macabi.	Pabillon.	Punta de Lobos.	Huanillos.	Independencia Bay.	Lobos Islands	Ichaboe.		Saldanha Bay.		Baker's Island.	Jarvis' Island.
											Old.	New.	Old.	New.		
Water,	12·36	13 67	17·94	21·41	29·07	11·59	8·11	18·01	8·69	19·96	27·30	16·98	22 03	12·18	10·00	11·80
Organic matter and ammonium salts,	59 92	52·05	48·21	39·03	39·06	39 89	30·81	36·22	34·62	18·73	34·30	48·22	14·93	35·51	9·20	8·20
Earthy phosphates,	17·01	22·78	22·18	24·60	23·37	26 98	35·96	24·81	20·13	42·59	30·30	22·76	56·46	12·78	75·15	—
Alkali salts,	7·20	9·67	9·86	10·81	6·59	15·65	20·23	16·66	13·62	10·92	7·10	3·25	5·04	9·09	—	—
Sand and silica,	3·51	1·83	1 80	4·15	1·90	5·89	4·89	4·30	22·94	7·80	1·00	8·79	1·54	30·44	·80	·50
Nitrogen,	17·38	13·61	12·65	9·86	10·93	8·79	5·95	7·77	7·89	3·55	6·01	12·06	1·21	9 00	·50	·40
Total phosphoric acid,	8·99	13·78	12·81	14 26	12·48	13·82	17·87	14·18	10·24	20·66	—	—	—	9 20	34 80	20 60
Soluble phosphoric acid,	1·20	3·34	2·65	3·76	1·78	1·47	1·41	2·82	1·02	1·38	—	—	—	3·34	·37	—

Angamos guano is a freshly deposited guano, collected in small quantities from ledges of rock; the analysis is that given by ANDERSON. The guano from the Chincha Islands has formed the great bulk of the imports during the last thirty years; the enormous deposits on the three islands are now exhausted. The composition given is the mean of seventy-eight analyses by WAY, representing cargoes received in 1852–55. This guano preserved almost to the end a very uniform composition. Ballestas, Guanape, and Macabi guano are deposits which have been worked since the exhaustion of the Chincha Islands; these deposits also are at the present moment almost or entirely consumed. These guanos contained much more water and less nitrogen than Chincha guano. The composition given for Ballestas guano is the mean of seventeen analyses by VOELCKER and one by BOCHMANN; that for Guanape guano is the mean of four analyses by VOELCKER and six by German chemists; that for Macabi guano is the mean of six analyses by VOELCKER. The South Peruvian guanos in present use are those of Pabillon de Pica, Punta de Lobos, Huanillos, and Independencia Bay: some is also brought from the Lobos Islands. The deposits on the first-named islands are by much the most extensive. The composition given for Pabillon guano is the mean of five analyses, that of Punta de Lobos of four analyses, that of Huanillos, Independencia Bay, and Lobos Islands, each of four analyses, all by VOELCKER. The South Peruvian guano is seen to contain an abundance of alkali salts, and to be generally poor in nitrogen; it is, however, much drier than the preceding importations.

The African guanos mentioned have been long exhausted, but fresh deposits are annually formed on the islands to a small extent. The analyses given of the old deposits are averages of the results obtained by URE, TESCHEMACHER, and WAY. The analysis of the new Ichaboe guano is the mean of two by VOELCKER. The analysis of the new Saldanha Bay deposit is the mean of three analyses by BOCHMANN and KROCKER. The new deposits are seen to be far more nitrogenous than the old; but from

their thinness are apt to be much contaminated with sand and stones.

The Baker, Jarvis, and Howland guanos are now nearly, if not quite, exhausted; they have principally been used in Germany. Jarvis' Island guano contained about 40 per cent. of gypsum, and a considerable part of the phosphoric acid existed as dicalcic phosphate. The analyses given are the averages adopted by E. Wolff; the soluble phosphoric acid is from Liebig.

The series of guanos in the table exhibits plainly their great variation in composition. In the Angamos guano we have the nitrogen twice the phosphoric acid; in the Baker's Island guano the phosphoric acid is about seventy times the nitrogen; this wide difference is probably simply owing to difference of climate. Guano has been obtained from many places besides those named, and notably from the west coast of America, both above and below Peru; but the individual deposits do not seem sufficiently important to merit notice. Several phosphatic guanos will be noticed by and by, under the head of materials used for superphosphate.

The better kinds of Peruvian guano usually contain about 1 per cent. of ammonia in the form of carbonate (in damp guanos the amount is larger), and about 5 per cent. of ammonia in other combinations; the bulk of the nitrogen occurs as uric acid and urates, but a small quantity exists as guanine, and a more considerable amount as insoluble humic compounds. The phosphoric acid exists for the most part as finely divided phosphate of calcium (bone earth), but a rather notable quantity is in the form of alkali phosphates, and consequently in a soluble state. Guano contains about 3½ per cent. of potash; soda, magnesia, sulphuric acid, and chlorine are also present. Guano, in fact, supplies not only large quantities of nitrogen and phosphates, but to a small extent many other elements of plant food. It is, however, chiefly important as a source of nitrogen. The nitrogen in guano readily becomes available as plant food, and may be reckoned as of equal value with the nitrogen of ammonium salts.

Peruvian guano is at the present time treated on a large scale with a small quantity of sulphuric acid, the guano being at the same time dried if necessary, and reduced to powder. This "dissolved guano" is prepared by Messrs. Ohlendorff, and is guaranteed to contain nitrogen equal to 9 per cent. of ammonia, 20 per cent. of soluble phosphates, and 4 per cent. of insoluble phosphates. By this treatment the volatile carbonate of ammonium is fixed, and a large quantity of the phosphate rendered soluble. According to A. Vogel a further effect of the sulphuric acid is to convert a great part of the uric acid into ammonia. A damp or lumpy guano thus treated is reduced to a fine powder. These considerable advantages are of course attended by an increase in price. The dissolved guano is largely used in Germany.

When guano is applied to land a considerable loss of ammonia may take place, according to Stöckhardt, if the manure is not thoroughly covered by the soil; this loss will be diminished in the case of dissolved guano.

Nitrate of Sodium.—This manure has hitherto held the second place to guano as a source of nitrogen to the farm, but the rapid exhaustion of the latter manure, and the uncertain quality of the deposits, are gradually securing for the nitrate a chief place in the farmer's attention. Nitrate of sodium is at present obtained from the Pampas, lying between Iquique and the Cordilleras in Peru. These Pampas are a table-land 3000 feet above the sea, and are almost entirely desert. The district worked for nitrate is about 20 miles wide and 75 miles long; the nearest point to the coast is about 10 miles distant. The surface of the Pampas is mostly covered with an indurated gravel known as "costra." Beneath this, lying not in strata, but in pockets or hollows, is the crude nitrate, called "caliche." Under the nitrate is a stratum of clay, often of great depth, known as "cova." The gravel varies in depth from about 1 to 4 yards, and may be said to average 1½ yard in thickness. The caliche is occasionally 4 yards in thickness, but averages three-quarters of a yard; if less than half a yard it is seldom worked. Caliche contains on an average 50 to 55 per cent. of real nitrate, but occasionally as much as 75 per cent.; qualities as low as 35 per cent. are worked. The principal impurity in caliche is common salt. The following analyses of caliche are by Dr. Machattie:—

	White Caliche.	Brown Caliche.
Water,	·99	5·64
Sodium nitrate,	70·62	60·97
" chloride,	22·39	16·85
" sulphate,	1·80	4·56
" iodate,	1·90	·73
Calcium sulphate,	·87	1·31
Magnesium sulphate,	·51	5 88
Insoluble matter,	·92	4·06
	100·00	100·00

The caliche is purified by boiling with water, or more generally with the mother liquor from a previous operation; the hot liquor is allowed to stand to deposit impurities, and is then run off for crystallization. As the solubility of nitrate of sodium is very different in hot and cold water, while the solubility of common salt is not greatly affected by temperature, this simple process suffices to purify the nitrate. The residue of the caliche which is thrown away is of course very rich in common salt; it also generally contains 20 per cent. of unextracted nitrate. Iodine is now prepared from the mother liquors in large quantity. *

Commercial nitrate of sodium is of standard quality when it contains 95 per cent. of real nitrate, inferior qualities may contain 90 to 92 per cent. The principal impurities are water and common salt. A little nitrate of potassium is generally present.

Nitrate of sodium of 95 per cent. will contain 15·65 per cent. of nitrogen, a larger quantity than is

* For many of the above particulars the writer is indebted to Flagg's paper in the *American Chemist*, iv. 403.

supplied in any ordinary guano. Nitrates contain nitrogen in the form most readily assimilated by plants; this fact, joined with the ready diffusibility of nitrates in the soil, renders nitrate of sodium the most powerful and rapid in action of all the nitrogenous manures at the farmer's disposal. Being of so soluble a nature, and being retained but slightly by the soil, it should only be applied in spring, when the plant is in a growing state, and ready to make immediate use of it.

The soda in this manure probably has no direct effect as a plant food; but by its action in the soil it appears to liberate phosphoric acid and potash from their combinations, and thus indirectly may be of material assistance.

Ammonium Salts.—The artificial supply of ammonia is but small, and is alone quite inadequate to meet the demands of the farmer for nitrogenous manure. Small quantities are obtained in the destructive distillation of animal matter, as in the preparation of animal charcoal; the greatest amount, however, is obtained from coal. The amount of nitrogen in coal varies from ·5 to rather more than 2 per cent. When coal is burnt, the greater part of the nitrogen is evolved as ammonia. Gas works are the principal sources of ammonia. The condensed water from the gas, and the ammoniacal liquor from the scrubbers, are more or less rich in ammonia; the quantity, however, varies very much according to the quality of the coal and the method of its treatment. Gas liquor may contain from 4 to 40 lbs. of ammonia per 100 gallons. The greater part of this ammonia generally exists as carbonate, a smaller quantity is present as hydrosulphate, hyposulphite, sulphate, chloride, and sulphocyanate of ammonium. In the case of some coals the amount of chloride of ammonium in the condensed water is very large, amounting to more than half the total ammonia. The water from the scrubbers contains, of course, nothing but volatile salts. The ammoniacal liquor obtained from bones is far stronger than that yielded by coal. Gas liquor is sometimes employed directly as a manure; in this case it should be considerably diluted with water before being applied to the land. Most generally, however, the liquor is distilled, and the ammonia collected in sulphuric acid, commercial sulphate of ammonium being thus produced.

The further purification of coal gas furnishes additional quantities of ammonia. When the gas is passed over hydrated ferric oxide (Hill's patent), for the purpose of removing sulphuretted hydrogen, the product contains both sulphate and sulphocyanate of ammonium. The mean of 102 analyses by J. Hughes, chemist to Lawes' Chemical Manure Company, gave 5·12 per cent. of sulphate, and 3·82 per cent. of sulphocyanate of ammonium. The spent oxide is washed to extract the ammonium salts, and the residue is used for the manufacture of sulphuric acid. A far better source of ammonia is, however, afforded when the gas is purified by sawdust soaked with sulphuric acid (Odling's patent); the product thus obtained contains when dry about 12 per cent. of nitrogen, equal to more than 50 per cent. of sulphate of ammonium. The whole of this nitrogen is not in the form of sulphate of ammonium, a part exists as cyanides and sulphocyanates; the proportion which these bear to the ammonia is, however, far smaller than in the spent oxide just noticed. By keeping the gas ammonia in bulk for some time it is said to lose sulphocyanic acid. This acid, being very volatile, is readily expelled if the gas ammonia is mixed with hydrochloric or sulphuric acid, and heat applied. Dry hydrochloric acid gas is very effective, and might perhaps be employed on a large scale for this purpose. Gas ammonia, if free from sulphocyanates, may be used at once as a manure; but if more than a trace of these salts be present it is dangerous to do so, sulphocyanates being highly poisonous to plants.

Commercial sulphate of ammonium is usually guaranteed to contain 24 per cent. of ammonia, equal to 93·18 per cent. of real sulphate. Samples containing a very large amount of nitrogen are probably contaminated with sulphocyanate. Sulphocyanate of ammonium contains 36·8 per cent. of nitrogen, which, calculated as ammonia, is 44·7 per cent.

Ammonium salts of all kinds are readily tested for sulphocyanates, by adding to their solution in water some ferric chloride; the formation of a blood-red colour shows the presence of sulphocyanates. If phosphates are present, hydrochloric acid must also be added to obtain the reaction.

Soot.—This manure is hardly worth mentioning, save that, as another nitrogenous manure derived from coal, it completes this part of the subject. House soot contains, according to Voelcker, about 1½ per cent. of ammonia, probably existing as sulphate; some kinds of soot yield, however, 4 to 5 per cent. of ammonia. A large part of common soot consists of coal ashes.

Woollen Refuse.—Woollen refuse has been long made use of as manure. Pure dry wool contains about 17 per cent. of nitrogen. Hair is equally nitrogenous. As hair and wool contain only about 2 per cent. of ash, they must be regarded as purely nitrogenous manures. Refuse wool is deteriorated in quality in proportion as it is associated with cotton and other fibres not nitrogenous, or is contaminated with oil, mineral dirt, and water. Way found in woollen rags (seams of old clothes) 10·47 per cent.; in premings, 9·92 per cent.; and in cuttings, 11·84 per cent. of nitrogen. The most abundant form of woollen refuse is shoddy. When first employed as a manure shoddy was rich in oil (Way found 26·35 per cent.) and in ash, and contained only 2 to 5 per cent. of nitrogen. Shoddy of a higher quality can now be purchased. The following analyses by Hughes show the composition of a good commercial article:—

	No. 1.		No. 2.
Water,	19·93	....	9·86
Organic matter,	63·40	....	76·68
Ash,	16·67	....	14·06
	100·00	....	100·00
Nitrogen,	6·83	....	7·92

By further care in removing dirt still higher qualities may be obtained. The writer has known clean shoddy to contain 9 to 10 per cent. of nitrogen.

As wool and hair suffer decay very slowly, their effect as manure is not immediate, but is spread over several years.

Blood is another nitrogenous manure of some importance. Perfectly dry blood will contain about 15 per cent. of nitrogen, and 4 per cent. of ash, of which about one-half is common salt; blood may therefore be classed among the purely nitrogenous manures. Blood is very retentive of moisture, and samples apparently dry may contain more than 20 per cent. of water. On the extent to which it has been dried the percentage of nitrogen greatly depends. The nitrogen in commercial dry blood usually varies between 10 and 13 per cent. Dried blood forms an excellent manure, but the difficulties of preparing it on a large scale have hitherto prevented its extensive use.

Flesh.—Dried flesh has been little used as a manure. There seems, however, some prospect of the solid residue obtained in South America and Australia from the manufacture of Liebig's extract of meat being utilized for this purpose. Three samples, recently imported from Australia, New Orleans, and South America, were found by Voelcker to contain 11 to 12 per cent. of nitrogen: the ash constituents were 3 to 8 per cent.

Fish.—Fish are occasionally caught in such immense quantities on the sea-coast as to be applied directly to the land as a manure, but fish manures are more usually prepared from the offal of fisheries. The following analyses show the composition of fresh sprats, and of dried Newfoundland cod. The sprats were analyzed by Way. These fish are occasionally used in large quantities as manure on the south-east coast of England. The analysis of cod fish is by Lawes and Gilbert.

	Fresh Sprats.		Dried Cod.
Water,	63·65	....	40·74
Oil,	18·60	....	·90
Nitrogenous matter,	15·65	....	39·70
Ash,	2·10	....	18·66
	100·00	....	100·00
Nitrogen,	1·94	....	6·60

The ash of fish consists chiefly of phosphate of calcium and phosphate of potassium. Way found in the ash of sprats 42 per cent. of phosphoric acid, 25·4 per cent. of lime, and 20·3 per cent. of potash.

Fish manures are usually very variable in composition, and should only be purchased on analysis. Sometimes they merely consist of dried fish refuse, at other times sulphuric acid has been added, and a part of the phosphate of calcium rendered soluble As an example of the former class of manures we will give the composition of Norwegian fish guano. This manure is of very constant composition. The figures given below are the mean of six analyses made by German chemists during the last twelve years, during which time the composition seems to have remained practically the same.

	Norwegian Fish Guano.
Water,	12·36
Organic matter,	52·91
Ash,	34·73
	100·00
Nitrogen,	7·84

This manure contains 28·9 per cent. of phosphate of calcium; the remainder of the ash is chiefly made up of salts of sodium and potassium.

Bone.—Bone is a very important manure, of which immense quantities are consumed by the farmer. Large quantities of bones are obtained from London and other great towns of the United Kingdom; they are also imported to a large extent. Formerly the principal imports were from the north of Europe; but improved means of communication have opened up other sources, and large quantities are now obtained from America, Africa, and other distant countries.

Bones are seldom used in their raw state; the fat is usually first extracted by steaming them for a short time. The average of seven analyses of commercial bones by Voelcker, and other English chemists, gives the following as their general composition:—

	Commercial Bones
Water,	11·06
Organic matter	30·48
Phosphate of calcium,	50·69
Carbonate of calcium and undetermined matter,	5·02
Alkali salts,	2·25
Sand,	·50
	100·00
Nitrogen,	3·61

Stohmann has remarked that the hard parts of bone contain more phosphate and less nitrogen than the soft parts; ordinary bone-dust, being obtained by sifting crushed bones, is chiefly derived from the soft tissue. Stohmann found in seven specimens of normal bone-dust a mean of 55·2 per cent. phosphate of calcium, and 3·44 per cent. nitrogen; while in seven specimens of bone-dust prepared from the soft parts of bone he found 44 per cent. of phosphate, and 4·14 per cent. of nitrogen.

Bones are boiled by glue-makers under pressure to extract the gelatin; such bones contain, of course, less animal matter, and a larger proportion of phosphate. Voelcker found in a good sample of boiled bones 60·48 per cent. of phosphates, and 1 84 per cent. of nitrogen.

The effect of bones as manure is only gradually manifested, as they undergo decomposition but slowly; they are of most use on light land, on clay they decay so slowly as to be almost ineffective. The smaller the bones are broken, the more speedy will be their action.

Animal Charcoal, resulting from the distillation of bones in close vessels, is employed in many manufactures for the purpose of decolorizing liquids; when it ceases to be efficacious in this respect it is sold to makers of superphosphate. The composition of the waste charcoal is most variable, depending on the purpose for which it has been used. It may

contain, according to R. Weber, 50 to 82 per cent. of phosphates, 5 to 10 per cent. of carbonate of calcium, 1 to 6 per cent. of free lime, 2 to 28 per cent. of sand, and 9 to 26 per cent. of water and carbon.

Bone Ash is chiefly obtained from South America: the proportion of phosphate of calcium it contains varies very much according to the amount of water and sand present, the percentage ranging from 60 to 82 per cent. It is usually sold on a basis of 70 or 75 per cent. of phosphate. The composition of pure bone ash from the mixed carcass bones of an entire ox, and the composition of a commercial sample were as follows:—

	Pure Ox Bone Ash.	Commercial Bone Ash.
Water and carbon,	1·86	6·70
* Phosphoric acid,	39·55	33·68
Lime,	52·46	43·37
Magnesia,	1·02	1·14
Oxide of iron,	·17	·58
Carbonic acid, alkalies, and substances not determined,	4·43	4·84
Siliceous matter,	·51	9·69
	100 00	100·00
* Equal to tricalcic Phosphate	86·34	73·52

The phosphates of guano, fish, bone, animal charcoal, and bone ash are all in a physical condition far more easily attacked by the natural solvents of the soil than is the case with crystallized, mineral, or fossil phosphates; the former may therefore be applied directly to the soil as phosphatic manures, but in the case of all, and especially of animal charcoal and bone ash, their efficacy will be much increased by treatment with sulphuric acid.

Superphosphate.—The gigantic manufacture of artificial manures in this country is based on the treatment of phosphates with sulphuric acid, by which the phosphate of calcium is decomposed, sulphate of calcium formed, and the phosphoric acid converted into a soluble acid calcium salt (a superphosphate), or else reduced to the free state. The suggestion to act on bones with sulphuric acid we owe to Liebig (1840); the utilization of crystalline and fossil phosphates by a similar treatment was the work of Lawes. His process for converting these hitherto valueless phosphates into manure was patented by him in 1842.

The reaction of sulphuric acid upon the tricalcic phosphate is in its simplest form as follows:—

$$Ca_3P_2O_8 + 2(H_2SO_4 + 2H_2O) = CaH_4P_2O_8 + 2(CaSO_4 2H_2O).$$

Here one molecule of tricalcic phosphate is acted on by two molecules of oil of vitriol and two of water, the result being one molecule of monocalcic phosphate and two of gypsum. This is a possible reaction, for it has been shown both by Piccard and Jones that two molecules of dilute sulphuric acid are sufficient to dissolve one molecule of tricalcic phosphate; but it is very doubtful if it ever occurs in practice. When a powdered phosphate is treated with sulphuric acid of the strength usually employed in making superphosphate (specific gravity, 1·55 to 1·60), great heat is evolved. If pure tricalcic phosphate is employed, and the mixture is made on a large scale, the temperature of the mass may, according to Kolb, rise as high as 150° C.; and in the ordinary manufacture the heat reached is always considerably above that of boiling water. Kolb has shown that samples of superphosphate, taken while the temperature is thus elevated, contain a large quantity of free phosphoric acid. He believes that the first reaction is as follows:—

$$6H_2SO_4 + 3Ca_3P_2O_8 = 6CaSO_4 + 4H_3PO_4 + Ca_3P_2O_8.$$

Free phosphoric acid is thus first produced, and this slowly reacts on the tricalcic phosphate as yet untouched, and forms monocalcic phosphate:—

$$4H_3PO_4 + Ca_3P_2O_8 = 3CaH_4P_2O_8.$$

If a pure and finely-ground phosphate is used, and a perfect mixture with the acid obtained, the second reaction is probably almost complete, so that the final result is the production of monocalcic phosphate by the action of two molecules of sulphuric acid on one molecule of tricalcic phosphate. In practice, however, the second reaction is rarely complete. A part of the tricalcic phosphate resists the action of the free phosphoric acid, and the resulting manure is found to contain some free phosphoric acid, as well as monocalcic phosphate; and, consequently, more than two molecules of sulphuric acid are found to have been consumed in rendering one molecule of tricalcic phosphate soluble. Kolb's theory is apparently sufficiently supported by facts. It has been shown by several chemists that the phosphates of calcium have a general tendency to split up into phosphoric acid and basic phosphates, when heated in the presence of water.

It has been supposed by some chemists that the diminution of soluble phosphate, which sometimes occurs in superphosphate when stored, is due to the reaction of monocalcic upon tricalcic phosphate, dicalcic or more basic phosphates being produced. It is quite plain that this can only happen when an insufficient quantity of sulphuric acid has been used, and an excess of unacted on tricalcic phosphate remains; this, however, will only be the case when the phosphate is badly ground, or solid bone is an ingredient of the manure. R. Jones believes that the drying of a superphosphate is attended with a decomposition of the monocalcic phosphate, phosphoric acid and basic phosphates being formed, and that here we have another cause of the reduction of soluble phosphate. According, however, to A. Millot, drying does not diminish the percentage of soluble phosphate. There is practically little or no reduction of soluble phosphate during the storing of a well made superphosphate prepared from finely ground and pure materials. In the presence of iron and aluminium a considerable reduction of soluble phosphate may take place after the manure is made; this reaction will be considered presently.

Before considering further points in the chemistry of superphosphate, it is necessary that we should have before us the composition of the phosphates actually employed by the manufacturer. In Table VIII. we have the composition of nearly all the phosphates employed in this country for the preparation of superphosphate; those only are excluded

TABLE VIII.—PERCENTAGE COMPOSITION OF PHOSPHATES EMPLOYED IN THE MANUFACTURE OF SUPERPHOSPHATE.

	Norwegian Apatite.	Canadian Apatite.	Spanish Phosphorite.		Bordeaux Phosphate.		Nassau Phosphate.		Cambridge Coprolite.	Suffolk Coprolite.
			Superior.	Ordinary.	Superior.	Ordinary.	Superior.	Good.		
Number of Analyses,.....	1	5	1	16	3	7	1	5	15	7
Water—Loss on ignition, ..	·90	·91	3·59	1·00	4·88	6·75	1·83	2·98	4·04*	4·40*
Phosphoric acid,.....	35·69	33·27	33·38	28·67	34·85	30·02	32·50	27·99	26·62	25·29
Lime,.....	46·39	45·56	47·16	40·60	46·92	37·89	48·18	39·39	43·30	39· 4
Magnesia,.....	·74	—	trace.	1·48*	·10*	—	—	·18*	·95*	·84*
Potash,.....	·36	—	—	—	—	—	—	·15*	·58*	·51*
Soda,.....	—	—	—	—	—	—	—	·18*	·64*	·87*
Ferric oxide,.....	1·29	—	2·59	·63*	5·63	—	2·91	5·88	2·18*	4·74*
Alumina.....	1·53	—	·89	·50*		—	1·26	4·02	2·05*	3·72*
Carbonic acid.....	none.	—	4·10	4·67*	3·91	—	1·91*	2·07*	6·82	5·27*
Sulphuric acid,.....	·29	—	·57	·90*	—	—	—	—	·91*	1·13*
Chlorine, ...	1·62	—	—	—	—	—	—	—	—	—
Fluorine, ...	—	—	—	·67*	—	—	—	4·88*	—	—
Siliceous matter,.....	11·62	10·38	3·71	20·92	2·65	7·51	2·46	12·01	8·19	10·98
Phosphoric acid, reckoned as tricalcic phosphate, .	77·90	72·62	72·87	62·59	75·97	65·53	70·95	61·10	58·11	55·20
Carbonate of calcium,.....	none.	—	9·31	10·62*	8·89	—	4·34*	4·70*	15·50	11·97*
Lime for 100 Phos. acid,. ..	130	137	141	142	135	126	148	141	163	155

	Potton Coprolite.	Boulogne Coprolite.	South Carolina Phosphate.			Sombrero Phosphate.		Navassa Phosphate.	Melillones Guano.	Malden Guano.
			River.	River Calcined.	Land.	Earlier Cargoes.	Later Cargoes.			
Number of Analyses,.....	7	13	13	48	11	5	4	8	3	3
Water, ...	3·35*	1·14*	4·96*	—	6·06	6·76	8·71	5·03	7·61	4·38
Loss on ignition,.....		2·60*		—		5·60		6·93	6·70	8·14
Phosphoric acid, ...	24·92	20·39	24·99	26·33	24·53	34·78	32·18	32·01	32·55	33·61
Lime,.....	33·64	32·50	40·15	40·55	37·95	37·97	45·76	36·54	36·94	43·22
Magnesia,.....	·15*	·58*	·49*	—	·60*	·46	—	·64*	3·08*	1·47*
Potash,.....	—	—	·07*	—	—	—	—	·56*	·44*	·18
Soda,.....	—	—	·69*	—	—	—	—	·38*	3·55*	1·32
Ferric oxide,.....	5·75	4·02*	2·23*	—	3·86*	3·11	—	4·37*	·52	·98*
Alumina,.....	3·50*	4·27*	1·28*	—	3·39*	5·83	—	8·94*	—	—
Carbonic acid.....	—	4·44	5·61*	5·17*	3·87*	1·46	6·55	2·45*	·86	5·48
Sulphuric acid,.....	—	1·03*	1·12*	—	1·84*	·45	—	·20*	4·44	·75
Chlorine,.....	—	—	·02*	—	—	·35	—	·16*	1·57	·95
Fluorine,.....	—	—	3·24*	—	—	—	—	none.	—	—
Siliceous matter,.....	15·30	26·41	13·48	12·74	14·15	1·54	·96	3·22	1·65	—
Phosphoric acid, reckoned as tricalcic phosphate,..	54·39	44·50	54·55	57·47	53·54	75·92	70·25	69·88	71·06	73·37
Carbonate of calcium,.....	—	10·10	12·75*	11·74*	8·79*	3·31	14·89	5·57*	1·84	12·45
Lime for 100 Phos. acid,. ..	135	159	161	154	155	109	142	114	114	129

of which the published analyses are too few, or too discordant, to allow of their average composition being ascertained. The object kept in view in constructing the table has been to represent as far as possible the composition of the bulks actually used in the manufacture, and not the composition of picked samples. Large use has, therefore, been made of commercial analyses, and the writer is much indebted to Dr. VOELCKER and to Mr. HUGHES, for the grant of some of their unpublished results. Analyses made for commercial purposes are usually incomplete, and express only the more important of the ingredients present. The figures given in the table for the smaller constituents are thus frequently the average of fewer analyses than the number stated at the head of the column; such figures are distinguished by an asterisk. In many cases no complete analysis of a phosphate has been found, and blanks consequently occur in the table; in these cases it must not be assumed that constituents are absent because no determination of them is recorded. The composition of bone and bone ash has been already given, and is therefore not repeated.

Apatite is the purest form of phosphate of calcium which is at the manufacturer's disposal. It is a definite chemical compound, consisting either of $3(Ca_3P_2O_8)CaFl_2$, known as fluor-apatite, or of $3(Ca_3P_2O_8)CaCl_2$, known as chlor-apatite, or else of these two united in indefinite proportions. The pure crystals of fluor-apatite will contain 42·26 per cent. of phosphoric acid, equal to 92·26 per cent. of tricalcic phosphate. The crystals of chlor-apatite will contain 40·92 per cent. of phosphoric acid, equivalent to 89·32 per cent. of tricalcic phosphate. These are the highest proportions of phosphoric acid which the manufacturer has to deal with.

The composition of *Norwegian Apatite* given in the table is from a single analysis by VOELCKER, and represents the average of a cargo from Krageroe. The Norwegian apatite is a chlor-apatite. It is

found in primitive rocks, and is consequently, when in bulk, more or less contaminated with siliceous matter; in picked specimens Voelcker found 90 per cent. of tricalcic phosphate. Norwegian apatite is little used in this country.

The composition of *Canadian Apatite* is the mean of five analyses by Voelcker, and represents cargoes of good quality. Apatite containing only 65 per cent. of tricalcic phosphate is occasionally imported. Canadian apatite contains fluoride, and sometimes carbonate of calcium; its chief impurity is siliceous matter. Rather considerable quantities of this phosphate are imported.

Spanish Phosphorite is really a fluor-apatite, more or less contaminated with quartz, and occasionally with limestone. It is found in large quantities in Estremadura, and in the neighbouring districts of Portugal. The principal deposits have been known for many years, but have only recently been largely worked. The analysis of the superior sample is by Voelcker. The composition given for the ordinary quality is the mean of twelve analyses by Voelcker, and four by Niederstadt. Cargoes occasionally contain less than 56 per cent. of tricalcic phosphate. A considerable quantity is imported.

Bordeaux Phosphate is the name by which the phosphate raised in the departments of Lot and Tarn-et-Garonne is known to English merchants. This phosphate does not resemble the apatites; it is of very various aspects and qualities. The composition of the superior phosphate given in the table shows it to contain a high percentage of phosphoric acid, with a somewhat considerable amount of oxide of iron and alumina, and some carbonate of calcium; but little fluorine is present. The higher qualities are now more rarely imported, and cargoes yielding less than 60 per cent. of tricalcic phosphate are not uncommon. These low quality phosphates contain much iron and aluminium, and are not suited for the manufacture of superphosphate. The analyses given are by Voelcker. Bordeaux phosphate is of quite recent introduction. A large amount has been imported to this country.

Nassau Phosphate, better known in England as "German Phosphate," is found in the valley of the Lahn, in Nassau. It was discovered in 1864, and a few years later was imported in large quantities. It varies from 30 to 70 per cent. of tricalcic phosphate. The best qualities form an excellent phosphate, but the amount of ferric oxide rapidly increases as the quality diminishes. Thus, while five cargoes, yielding 61 per cent. of tricalcic phosphate, contained 5·88 per cent. of ferric oxide, and 4·02 per cent. of alumina, the average of seven other cargoes received about the same time, but yielding only 56 per cent. of tricalcic phosphate, was 7·17 per cent. of ferric oxide and 4·07 per cent. alumina. The low qualities of Nassau phosphate are quite unfit for the manufacture of superphosphate. They are sometimes used in Germany without treatment with sulphuric acid, being made into a compost with farmyard dung, turf, leaf mould, &c., and applied in this state to the land. Of the higher qualities but little is raised, and the total imports to England have much diminished. Nassau phosphate is remarkable for containing a distinct amount of iodine; when treated with sulphuric acid on a large scale violet vapours are frequently produced. The analyses in the table are by Warington; the determinations marked with an asterisk in the composition of the second-class phosphate are by Dietrich and König.

Phosphatic nodules and fossils of various kinds, known as coprolites, are found in many parts of England and the Continent; they occur in very various geological strata. Only those deposits are worked which are of sufficient size, and are tolerably rich in phosphoric acid.

Cambridge Coprolite is of all English coprolites the best suited for the manufacture of superphosphate, being both richer in phosphoric acid, and containing at the same time a smaller amount of objectionable impurities than is found in other deposits. The coprolites are raised from the Upper Greensand of Cambridgeshire and Buckinghamshire; they are of a grey or greenish tint; the large coprolites are of a better quality than the small ones. In Cambridge coprolites the iron does not exist as ferric oxide, or only so to a small extent, but is present as pyrites and ferrous silicate—forms which we shall presently see are far less prejudicial to the manufacturer than ferric oxide. Cambridge coprolite contains much more carbonate of calcium than other coprolites. All coprolites contain fluorine. The composition given in the table is the mean of eleven analyses by Hughes, three by Voelcker, and one by Richter. These coprolites have for many years formed the staple material of the English manufacturer.

Suffolk Coprolites.—These are raised in Suffolk and some adjoining counties; they are of tertiary origin. Suffolk coprolites were the coprolites first employed in the manufacture of superphosphate, and for about fifteen years were the principal material used. These coprolites are of a reddish brown colour. They are poorer in phosphoric acid and richer in iron than the Cambridge coprolites; the iron is also to a considerable extent present in the ferric state. They are not suitable for the preparation of a high class superphosphate, but are now employed for mixing with other materials. The composition given is the mean of four analyses by Hughes, two by Voelcker, and one by Warington.

Potton Coprolite is raised in Bedfordshire; it occurs in the Lower Greensand formation. These coprolites are of a red colour; they are inferior to the Suffolk in quality. The best and largest coprolites contain as much phosphoric acid as good Cambridge coprolite, with considerably less lime, and much more ferric oxide. The smaller coprolites are very inferior, containing about 48 per cent. of tricalcic phosphate, with a large amount of iron. The composition given in the table represents coprolite of good quality; it is the average of five analyses by Warington, one by Voelcker, and one by Richter.

Boulogne Coprolite has been used lately for mixing with materials of higher quality; it is of a grey colour, and occurs in the Upper Greensand. In

composition it is very similar to the coprolites found on the English coast at Folkestone. Boulogne coprolite is poor in phosphoric acid; but its principal impurity being siliceous matter, it yields better results to the manufacturer than richer phosphates contaminated with ferric oxide. The composition given is the mean of eight analyses by Hughes, and five by Voelcker.

South Carolina Phosphate, also known as Charleston Phosphate, differs in external character from coprolite, though of a similar composition. It occurs in rough masses, largely perforated by boring mollusca, and associated with fossil bones and teeth. The river phosphate is of a dark-grey colour, the land phosphate of a pale brown. Carolina phosphate is apparently a converted Eocene marl. It was long known to geologists, but its commercial value was not recognized till 1867; since then immense quantities have been raised and exported to England. The cavities in the phosphate are naturally filled with sand and clay, and it requires careful washing; when this washing is imperfectly performed the phosphate is of lower quality. The river phosphate is obtained by dredging in the Bull, Soosaw, and Stono rivers; it is the kind chiefly imported to England. River phosphate is much harder than the land phosphate, but is of superior quality for the purpose of manufacturing superphosphate. In the river phosphate the iron exists partly as pyrites; thus, out of the 2·23 per cent. of iron reckoned as ferric oxide, given in the table, 1·04 existed as pyrites. In the land phosphate the iron is apparently in the ferric state. River phosphate is now dried by hot-air flues before exportation, and is then known as calcined phosphate. Carolina phosphate is very uniform in composition. Though containing generally rather less phosphoric acid than good Cambridge coprolite, the river phosphate is distinctly superior to coprolite as a material for superphosphate; the lower amount of carbonate of calcium present allowing a smaller proportion of sulphuric acid to be used, and the phosphate being of a nature more easily attacked by acid. The land phosphate is of less value, and yields a lower percentage of soluble phosphate. The analyses of the river phosphate are by Warington, those of the calcined phosphate by Hughes, and those of the land phosphate are the average of seven by Voelcker and four by Warington. The determinations of magnesia, potash, soda, chlorine, and fluorine, in river phosphate, are from a single analysis by Fresenius. The determinations of carbonic acid in all three phosphates are chiefly from analyses by Cripps.

Sombrero Phosphate is one of the numerous phosphates which are obtained from the coral islands of the Caribbean Sea. These phosphates are frequently called Rock Guanos; their origin is, however, in several cases very obscure. Sombrero phosphate is of high quality, containing sometimes, however, a good deal of alumina; the later importations contain much carbonate of calcium. The phosphate is rapidly approaching exhaustion. The analyses given are by Voelcker.

Navassa Phosphate is another of the West Indian phosphates; it has a well-marked pisolitic structure, and is of a bright red colour. This phosphate contains phosphoric acid equal to from 60 to 70 per cent. of tricalcic phosphate, a moderate amount of carbonat of calcium, a rather considerable quantity of iron, and a large amount of alumina. The latter is its distinguishing feature, and prevents its successful employment for high-class superphosphates. Like the other phosphates of its class it contains no fluorine. Large quantities of this phosphate have been imported to England. The composition given is the mean of four analyses by Voelcker, and one each by Bretschneider, Gilbert, Ulex, and Warington

The chief of the other Caribbean islands yielding phosphates are *Maracaibo* or Monk's island, from which a phosphate of very high quality, formerly employed in the manufacture of Lawson's Phospho-guano, was obtained, but which is now apparently exhausted; *St. Martin's* island, yielding at the present time an excellent phosphate, but apt to be contaminated with a large proportion of carbonate of calcium; *Curaçao* island, also producing an excellent phosphate; *Aruba* island, yielding a phosphate of variable quality, and sometimes containing much iron and aluminium; *Pedro Keys* island, and others of less importance.

Mejillones Guano is obtained from the coast of Bolivia; it is a phosphate of high quality, very free from impurities hurtful to the manufacture of superphosphate. It is at present largely used for the preparation of "Biphosphated Guano." The analyses given are by Voelcker. Besides the ingredients mentioned in the table the phosphate contained an average of ·89 per cent. of nitrogen.

Baker, *Jarvis*, *Howland*, *Malden*, and *Starbuck* islands belong to the Pacific Ocean group. Most of these phosphatic guanos have been largely used in Germany for the preparation of high-class superphosphates. The two former islands are now almost exhausted; the composition of their guanos has been noticed already under the head of *Guano*. The Howland phosphate is still used for the manufacture of phospho-guano. The analyses of Malden guano are by Fittbogen, Krocker, and Von Grote. This guano contained ·43 per cent. of nitrogen.

We have now before us the composition of the principal phosphates employed in the manufacture of manure; we see that they contain besides tricalcic phosphate a variety of other ingredients. The reaction of sulphuric acid with pure tricalcic phosphate has been already considered; we have now to notice the reactions which are determined by the presence of the other ingredients of mineral phosphates.

It is evident, in the first place, that all carbonate, fluoride, and chloride of calcium present will be attacked by the sulphuric acid used, that sulphate of calcium will be produced, and carbonic, hydrofluoric, and hydrochloric acid expelled in the form of gas. This action is much aided by the high temperature which the mass reaches after the addition of sulphuric acid. It of course follows that

when any of these calcium salts are present, a larger amount of sulphuric acid must be used to render the phosphate soluble than is required by the amount of phosphate of calcium present, and that the resulting manure will contain an excessive quantity of gypsum over that yielded by pure tricalcic phosphate. This dilution of the product with gypsum naturally reduces the percentage of soluble phosphate present, while the increased amount of sulphuric acid consumed by no means conduces to economy of manufacture. On the other hand, the evolution of gas insures a light porous texture in the manure—a point of very great importance; and the extra quantity of gypsum formed increases the dryness of the product. The presence of a small quantity of carbonate in a phosphate is on the whole certainly advantageous to the manufacturer; excessive quantities are plainly injurious. Fluorides and chlorides, especially the former, are sources of great annoyance from the irritating nature of the gases evolved.

At the foot of Table VIII. the proportion of lime to phosphoric acid in each of the natural phosphates has been given; this will generally give a fair idea of the proportion of calcium salts other than phosphate present. In cases where the mineral contains sulphate of calcium, the amount of sulphuric acid required will, however, be less than would follow from these figures. In pure tricalcic phosphate the proportion of phosphoric acid to lime is 100 : 118; in pure apatite the proportion is 100 : 131.

Magnesia, and salts of the alkalies, are usually present in quantities too small to possess much influence; they are most abundant in guanos.

Ferric oxide and alumina are ingredients of the greatest moment to the superphosphate manufacturer. Phosphates containing iron and aluminium have generally a part of their phosphoric acid in union with these bases. This is plainly the case in some phosphates containing much iron and aluminium. Thus in Sombrero and Navassa phosphates there is clearly less lime than is required to form tricalcic phosphate with the phosphoric acid present; and we must either conclude that a part of the phosphate of calcium is more acid than tricalcic phosphate (which is improbable, as both minerals contain carbonate of calcium), or that a portion of the phosphoric acid is united to aluminium or iron. Phosphate of iron and aluminium are only soluble in the presence of much free acid, and are never found, save in very small quantity, in the aqueous solution of ordinary superphosphates; they are thus valueless for the production of soluble phosphate. The *Redonda* and *Alta Vela* phosphates are examples of minerals rich in phosphate of aluminium, but quite useless to the maker of superphosphate.

The larger portion of the iron and aluminium in ordinary phosphates is, however, not combined with phosphoric acid; unfortunately, it does not remain so. If a phosphate containing free ferric oxide, as Nassau or Navassa phosphate, is treated with sulphuric acid on a large scale, the red colour of the phosphate is seen to disappear shortly after mixing, and the mass becomes white. If samples of the mass be taken immediately after mixing, and again after the red colour has gone, it will be found that in this short time the amount of soluble phosphate has greatly diminished. The rapidity with which the red colour disappears depends greatly on the temperature of the mass. Thus if similar proportions of phosphate and acid are mixed, and the mass in one case be broken and spread out to cool immediately it has set, and in the other case be covered and allowed to retain its heat for twelve hours, it will be found that under the first conditions a red manure is produced containing far more soluble phosphate than the white manure obtained by working on the second plan. In an experiment made with Nassau phosphate mixed with 85 per cent. of sulphuric acid, sp. gr. 1·6, the mass weighing about 14 cwts., it was found that if broken up and cooled as soon as set the manure contained 23·75 per cent. of soluble phosphate, while if left untouched for eighteen hours the amount of soluble phosphate was only 13·55 per cent. The temperature of the mass at the end of eighteen hours was still 70° C. A similar experiment made with Navassa phosphate mixed with its own weight of sulphuric acid, sp. gr. 1·6, yielded, after half an hour's standing, 30 per cent. of soluble phosphate, and after twelve and a half hour's standing 25·8 per cent. of soluble phosphate; the temperature of the mass was then 82°. When ferruginous phosphates are mixed with sulphuric acid on a small scale by means of a pestle and mortar, any rise of temperature being prevented by standing the mortar in cold water, ar higher amounts of soluble phosphate are obtained than by mixing the same proportions in bulk. This striking influence of heat in promoting the formation of ferric and aluminic phosphate is doubtless due, not only to the greater activity of re-agents at a high temperature, but also to the fact, already noticed, that at a high temperature free phosphoric acid is largely formed, while in the cold the product is chiefly monocalcic phosphate. The free phosphoric acid would doubtless attack ferric oxide and alumina with far greater energy than an acid calcium salt would be capable of exerting.

The facts just described naturally suggest the treatment of ferruginous phosphates in the cold, or at least with as short an exposure to heat as possible. The latter method has been tried by Lawes, but is unfortunately only temporarily successful. The manure is at first much richer in soluble phosphate than that prepared in the ordinary way; but it gradually deteriorates, and a few months' keeping is found to produce the same effect as a few hours' exposure to a high temperature. The mechanical condition of the manure made with little heat is also inferior to that prepared in bulk at a high temperature. The writer believes, however, from his experiments, that if a manure could be made in the cold with a minimum of acid, and brought to a sufficiently *dry* condition, it would remain for any length of time unaltered: but if moisture or excess of acid be present the iron is sure to be gradually attacked. The difficulty, however, of preparing a thoroughly dry manure by treatment in the cold is very considerable.

The behaviour of alumina differs in some important respects from that of ferric oxide. Superphosphate made from Navassa, and allowed to remain hot, quickly loses its red colour; but the reduction of the soluble phosphate by the alumina takes a much longer time. Till the reduction is nearly completed the manure is of an extraordinary gluey consistence, and if treated with cold water large quantities of alumina pass into solution; but after the heat has long continued the manure becomes dry and pulverulent, and when treated with water but little alumina is dissolved. This change takes place through the whole mass of the manure, and is not connected with any loss of water. Whether an acid phosphate of aluminium is first formed, which afterwards becomes basic by acting on the remaining alumina, or whether some other explanation is the true one, it is difficult to say.

The reactions just described are in their results well known to manure manufacturers. The manure is said to "go back," and the soluble phosphate to become "reduced."

Supposing the ferric oxide and alumina of a phosphatic mineral to be entirely converted into normal phosphates in the manufacture of superphosphate, then 100 parts of ferric oxide will render 88·7 of phosphoric acid insoluble, equivalent to a loss of 194 of soluble phosphate; and 100 parts of alumina will render 137·8 of phosphoric acid insoluble, equal to a loss of 300 of soluble phosphate.

The form in which the iron and aluminium are present doubtless influences their action towards the phosphoric acid. Iron pyrites is insoluble in acids, and has probably no effect on the manure. Ferrous silicates have also probably but little action. The iron of French and Cambridge coprolite, and of the Carolina river phosphate, is thus comparatively harmless. Free ferric oxide is, on the other hand, actively injurious.

Sand is the most innocent of all the useless ingredients of mineral phosphates; it consumes no acid, it does not reduce the soluble phosphate, it is simply inert. Sandy phosphates are thus often of more value than would appear from their analysis. The writer has known a poor Folkestone coprolite, containing 45 per cent. of phosphate and 30 of sand, when treated with the small amount of acid which it required, to yield a manure containing a larger percentage of soluble phosphate than was obtained by working a 70 per cent. Navassa phosphate on a large scale.

The composition of a phosphate being known, it is, of course, possible to calculate the quantity of sulphuric acid which will be required to render the phosphate soluble. To do this we must assume that the reactions will proceed in a certain manner. If we suppose that monocalcic phosphate will result from the action of the sulphuric acid on tricalcic phosphate, and that ortho-phosphate of aluminium and iron will result from the reaction with the oxides of these metals, we may proceed as follows:—Reckon first all the phosphoric acid as tricalcic phosphate; an excess of lime will usually remain. If, however, an excess of phosphoric acid is found, calculate its equivalence in alumina, and deduct this alumina from the amount present. We have then to find the amount of sulphuric acid required by the tricalcic phosphate, excess of lime, ferric oxide, and alumina. On the assumption already made it is only necessary to reckon one molecule of sulphuric acid for each molecule of alumina and ferric oxide, as the sulphuric acid calculated for the other constituents is sufficient to convert all phosphoric acid into monocalcic phosphate, and

$$CaH_4P_2O_8 + Al_2O_3 + SO_3 = CaSO_4 + Al_2P_2O_8 + 2H_2O.$$

The magnesia and alkalies present may generally be left out of consideration; if, however, they distinctly exceed the amount of sulphuric acid naturally present in the mineral they must, of course, be included in the calculation. In phosphates containing sulphate of calcium, the lime thus combined must be subtracted from the excess of lime before reckoning its equivalent in acid. The data given in the following table will suffice for most of the phosphates used by the manufacturer. It is assumed that chamber acid of 1·6 specific gravity contains 55 per cent., and acid of specific gravity 1·55, 51·5 per cent. of sulphuric anhydride:—

TABLE IX.—RELATION TO SULPHURIC ACID OF THE VARIOUS INGREDIENTS OF MINERAL PHOSPHATES.

100 Parts require.	Sulphuric Anhydride. (SO_3).	Sulphuric Acid. Sp. Gr. 1·60.	Sulphuric Acid. Sp. Gr. 1·55.
Tricalcic phosphate,....	51·6	94	100
Excess of lime,.....	142·8	260	277
Ferric oxide,.....	50·0	91	97
Alumina,.....	77·6	141	151

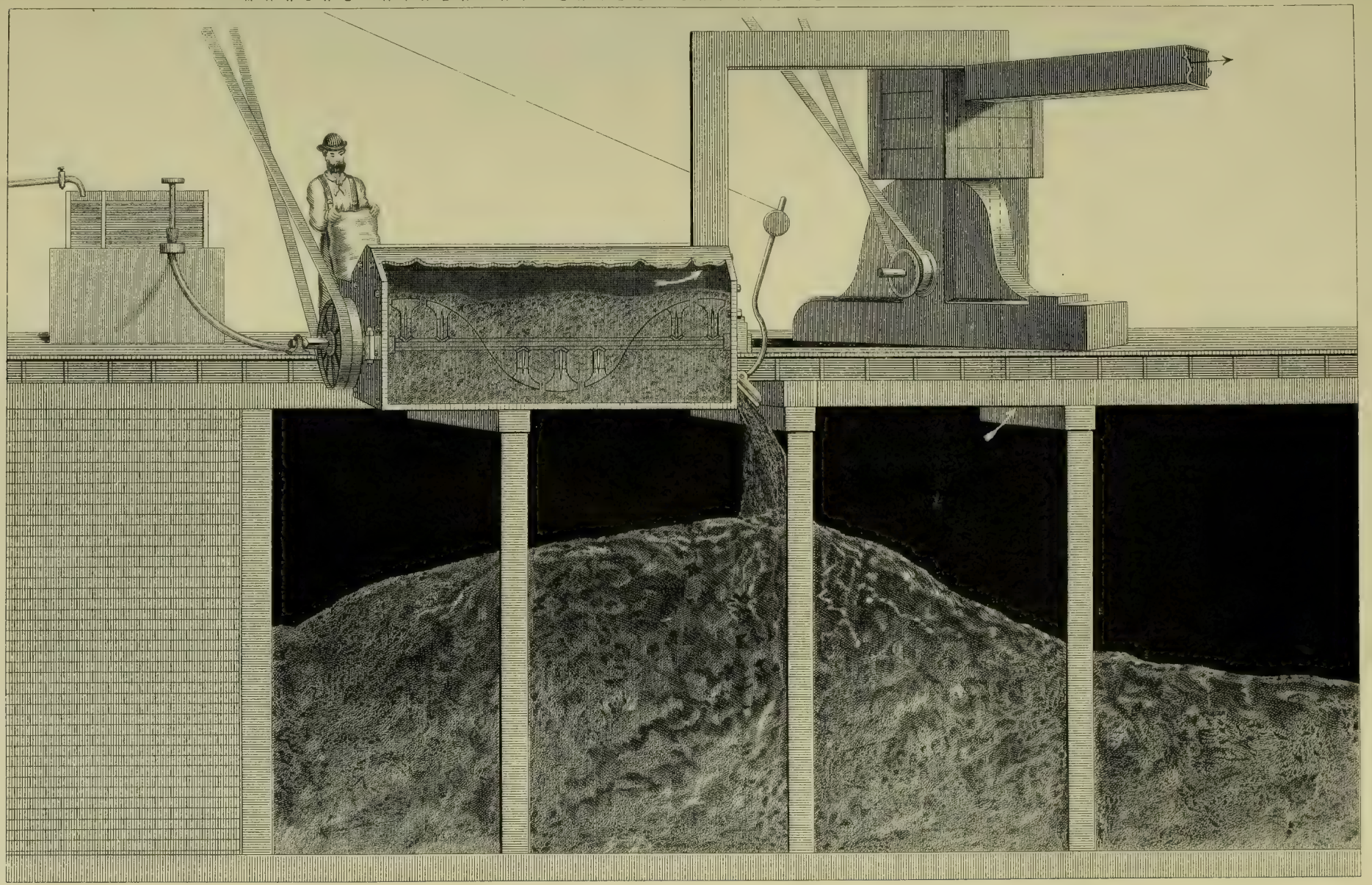
In cases in which the phosphoric acid is in excess of the lime a further figure will be required:—

100 phosphoric acid = 72·5 alumina.

A calculation made from these data may possibly give too little acid, as in practice some free acid is generally found in superphosphate; but will more probably err in the other direction, as a part of the mineral generally escapes the action of the acid. A manufacturer in practice will generally use as much acid as is consistent with a dry product, but it is well to check the work by a calculation such as has been just described.

Another point to be considered is the proper strength of acid to be employed. If tricalcic phosphate is acted on by sulphuric acid with a view to form monocalcic phosphate ($CaH_4P_2O_8$) and gypsum ($CaSO_4 2H_2O$), then it is clear that the sulphuric acid must be $H_2SO_4 + 2H_2O$, corresponding with a specific gravity 1·65. The same strength of acid would theoretically be required to produce free phosphoric acid ($H_6P_2O_8$) and gypsum. If, however, we assume with Joulie that monocalcic phosphate can only exist in a hydrated state, having the formula $CaH_4P_2O_8,2H_2O$, it then becomes necessary to employ $H_2SO_4 + 3H_2O$ to insure its formation. Sulphuric acid of this formula has the specific gravity

MANURE MIXER AT LAWES' CHEMICAL MANURE FACTORY.



1·55. If the acid is to act on carbonate or fluoride of calcium, sulphuric acid, $H_2SO_4 + H_2O$, specific gravity 1·78, will theoretically be the proper strength to insure the formation of gypsum. As to the strength of the acid proper to act on phosphates containing iron and aluminium, nothing can be said, as little is known as to the hydration of the ferric and aluminic products.

On the whole, it may be concluded that pure sulphuric acid of the gravity 1·55 is the normal strength for acting on pure phosphates; but that in the case of phosphates containing much excess of lime, as Cambridge coprolite, a somewhat greater strength may be advantageously employed. It must be recollected that the chamber acid used by manure-makers is always weaker than its gravity indicates, as the gravity is increased by the impurities present. Acid somewhat denser than 1·55 will thus be equal to this gravity in pure acid.

A point of great importance for the successful preparation of superphosphate is the fine grinding of the materials; unless the phosphate is reduced to a very fine powder, the action of the acid will be incomplete. The following results obtained with Nassau phosphate in various conditions of fineness, but treated in every case with the same proportion of acid, will illustrate the subject:—

Fineness of Dust.	Soluble Phosphate obtained.
Passed through 38-wire sieve, ...	22·65
" 50-wire sieve, ...	23·80
Finest powder which could be ground, ..	25·75

No dust should be used which does not pass through a sieve of forty wires to the inch, and in the case of hard phosphates still finer grinding is very desirable. Bone is never reduced to powder when used as an ingredient of superphosphate, but is merely broken into half or quarter inch pieces; the dust formed in crushing the bones being sifted out and sold as bone dust. The object of the manufacturer is that the bone shall *appear* in the manure. This is done solely to please the eye of the consumer, who is satisfied that bone has been used if he sees it visibly present. The result of this practice is that the phosphate of the bone is very partially acted on by the acid, and such superphosphates are apt to diminish in soluble phosphate by keeping.

The richness of the superphosphate produced depends, of course, primarily on the quality of the phosphate used, and the completeness with which it is acted on. The highest quality of superphosphate is usually prepared from phosphatic guanos: the guano of Mejillones, Howland, and Malden island are used at present for this purpose. Such guanos, containing no excess of lime, require but little acid in relation to the phosphate present; and being almost free from iron and aluminium there is no difficulty in rendering the whole of the phosphate soluble. With such materials it is possible to obtain superphosphates containing 40 to 45 per cent. of soluble phosphate.* Bone ash is another excellent phosphate, and one readily attacked by acid; it contains, however, a small excess of lime. Bone ash will yield superphosphates containing 35 to 40 per cent. of soluble phosphate. Many other of the high quality phosphates mentioned in Table VIII. also yield manures rich in soluble phosphate. Of the more ordinary and more largely used phosphates, Carolina river phosphate is the best, 30 per cent. of soluble phosphate being readily obtainable. With Cambridge coprolite 25 per cent. of soluble phosphate is about the average, but with selected coprolites and fine grinding this may be raised to 27 per cent. Bone is perhaps of all the ordinary phosphates the one that yields the least soluble phosphate; it contains but a low percentage of tricalcic phosphate, and this in a condition which is with difficulty attacked by acid.

In making most superphosphates a mixture of ingredients is employed. It is usually desired to produce a manure containing a certain definite percentage of soluble phosphate; with this view it is common to mix together a higher and lower quality of phosphate. High quality phosphates are for the same reason sometimes also diluted by mixture with gypsum. The massive selenite of Rouen is largely used for this purpose.

Another reason for mixture is the desire to introduce nitrogen into the manure. To attain this object the ground phosphate is mixed with bone, shoddy, or crude ammonium salts, and the whole mixture treated with sulphuric acid. The manures resulting from such mixtures are known as Dissolved Bones, and Turnip Manure. Ammonium salts containing sulphocyanates are especially suitable for use in this manner. These impure salts, if applied directly to the land, would kill the crop; but when mixed with sulphuric acid, and subjected to the heat of the manure pit, the sulphocyanic acid is volatilized, while all the ammonia is retained.

Superphosphate was in its earliest days made by hand; various forms of machinery have since been employed to effect the mixing. One of the simplest and best forms of apparatus is that made by Messrs. Turner of Ipswich. On Plate I. is an engraving of one of these mixers. The drawing represents the mixing machinery in use at the Barking Factory of Lawes' Chemical Manure Co. The sketch has been taken by their kind permission.

The pit to receive the manure occupies the lower part of the Plate; it is shown in section, and extends to the right much further than is represented in the drawing. The pit is a chamber about 33 feet long, 19 feet wide, and 11 feet high. The sides and the back end are formed of brick walls, the front end is closed by boards when the pit is being filled. The pit has a permanent wooden roof, supported by the side walls, and by a series of wooden posts (shown in section), which pass down the centre of the pit. The pit is made tolerably air-tight by packing all crevices before mixing commences.

The mixer, with its Archimedean screw, is shown in section. The frame of the mixer is made of wood, the screw of iron. At the left extremity of the

* The term "soluble phosphate" is universally used for the soluble phosphatic matter in superphosphate; by this phrase monocalcic phosphate is not meant, but *tricalcic phosphate rendered soluble.*

mixer is a hopper for introducing the powdered phosphate, known as "dust;" in the drawing the hopper is behind the mixer. At the same extremity is the pipe which delivers the acid to the mixer. The acid tank is seen on the extreme left; it is filled from a cock attached to the main. The tank is made of wood, lined with lead; it is provided with a gauge, by which the quantity of acid used is determined; the exit pipe from the tank is closed by a plug attached to a long handle. When mixing is to commence, the charge of dust being already weighed in bags, and the tank filled to the proper mark on the gauge, the mixing screw is set in action, and the delivery of acid and dust proceeded with simultaneously. As soon as all the materials are run in the cord is drawn which opens the valve at the right end of the mixer, and the whole charge is by the continued motion of the screw turned out into the pit. The artist has represented the mixer as being both charged and discharged at the same time, in order to show every part in action; of course, in practice, charging does not recommence until the exit valve has been again closed. A charge consists of 15 cwts. of material. The operation of charging and mixing is very brief, so that 10 tons of manure are easily made in one hour, and a considerably larger amount can be made by brisk working. The manure when discharged is sufficiently fluid to run pretty equally over the pit; it sets in less than an hour. A pit of the size named will hold when fairly filled about 120 tons of manure.

To the right of the mixer is seen the ventilating apparatus designed to carry off the gases evolved. The air in the ventilating shaft is put in motion by a fan worked by the bands shown in the plate. The ventilating shaft is connected both with the mixer, to remove the gases given off during mixing, and also with the pit; the ventilating shaft from the pit is shown in dotted lines only, as it would obstruct the view of the principal shaft. At the Barking Factory there are several pits side by side, each with its own mixer; but there is only one acid tank, and one ventilating shaft for the series, each mixer having its own connection with the shaft and tank. Only one mixer is used at a time. The ventilating shaft is made of wood, covered with pitch on the inside.

The gases given off during mixing are carbonic acid, fluoride of silicon, hydrochloric acid, and water, and under some circumstances iodine and sulphocyanic acid. Most of these gases are extremely irritating to the lungs, and very injurious to health; their perfect removal is a vital necessity. The gases are conducted by the ventilating shaft to a small water tower, filled in some cases with coke; here the acids are condensed by a stream of water, and the gas is rendered fit to enter the atmosphere.

A curious deposit takes place in the ventilating shafts; they become after a time so completely choked with white flakes, which grow out from all sides, that they have to be taken down, cleaned, and replaced. These white flakes consist of silica, moistened with solution of hydrofluosilicic acid. Their origin is simply explained. The mixed water vapour and fluoride of silica evolved by the manure, decompose each other as they pass through the shaft, silica is deposited, and hydrofluosilicic acid formed.

The manure when thoroughly set is removed from the pits at the end temporarily closed with boards; it is broken down with picks, and may be at once put into bags. If, however, the manure is to be sown by drill the lumps must be broken, and the whole reduced to a fine powder; this is done by passing the manure through a sieve or screen, or by the use of Carr's disintegrator.

The character of superphosphates has greatly improved of late years, from the employment of better phosphates, finer grinding, acid of proper strength, and more effective methods of mixing. Way, writing in 1855, states as the result of his examination of 171 samples of superphosphate in the preceding three years, that

6½	per cent.	contained less than 5	per cent. soluble phosphate.
29	"	from 5 to 10	"
35	"	" 10 to 15	"
23	"	" 15 to 20	"
6½	"	more than 20	"

He adds, "I am inclined to adopt 15 per cent. (as I have done for some years) as a fair average for a well-made article." It is only fair, however, to add that he is speaking of manures containing some nitrogen, and states that on an average 1 per cent. of ammonia will also be present. At the present time turnip manures with one-half to 1 per cent. ammonia are readily procured, containing 23 to 25 per cent. of soluble phosphate, while cheap mineral superphosphates with 25 to 27 per cent. soluble are equally common. Higher priced articles may be obtained of almost any quality.

When a superphosphate is to contain much nitrogen, the nitrogenous material is usually added after the superphosphate has been made; this is a necessity if the nitrogenous matter is of a bulky character, or if nitrate of sodium is to be employed. The substances added to superphosphate, for the preparation of mixed manures, are generally crystallized sulphate of ammonium, Odling's gas ammonia, nitrate of sodium, dried blood, or shoddy and other inferior materials. If a highly concentrated manure is to be prepared, crystallized sulphate of ammonium must be employed, this being the material richest in nitrogen at the manufacturer's command; for ordinary mixed manures nitrate of sodium or crude ammonium salts are largely employed.

Mixtures of ammonium salts and superphosphate are very satisfactory and permanent; the mixtures with nitrate of sodium are permanent only when carefully made. If nitrate of sodium is mixed with a high quality superphosphate that is at all damp, the nitrate is apt to be attacked by the acid of the manure, red fumes are evolved, the mass becomes very hot, and great mischief may ensue. This is especially the case if the proportion of superphosphate is large in proportion to the nitrate. The difficulty may be avoided by adding a very small quantity of sifted slaked lime, or some dry gypsum, when the

mixture is made. Ammonium salts and nitrate of sodium should on no account be employed in the same manure. The mixture of sulphate of ammonium and nitrate of sodium is very hygroscopic (nitrate of ammonium is evidently formed); the heating of the mixture in the presence of superphosphate is also more energetic than with nitrate only.

The ingredients of mixed manures are united by passing them through a screen, or through Carr's disintegrator. These mixed nitrogenous manures are known as "wheat," "barley," "mangold," and "potato" manures. If intended for autumn application nitrate of sodium should not be employed in such mixed manures; for spring manures it is a most valuable ingredient.

Having described the manufacture of superphosphate, and of kindred artificial manures, we must add a few words as to the manurial value of their constituents.

Superphosphate supplies to the soil large quantities of phosphoric acid, sulphuric acid, and lime, and in the case of a mixed manure also some nitrogen. In analyses of superphosphate the phosphoric acid is given in two forms—as soluble, and as insoluble phosphate. The soluble phosphate, we have already seen, consists of monocalcic phosphate with some free phosphoric acid. When applied to the land the soluble phosphate is dissolved by rain, and distributed more or less throughout the surrounding soil. When thus brought in contact with fertile soil, the soluble phosphate is more or less speedily precipitated. This precipitation is brought about either by the carbonate of calcium of the soil, or by the hydrated ferric oxide and alumina present. In the first case a more or less insoluble phosphate of calcium, and in the second case a basic phosphate of iron or aluminium, is produced. In all soils containing ferric oxide and alumina it would appear that even when the first precipitation is brought about by calcium carbonate, yet by slow degrees the greater part of the phosphoric acid is transferred to iron and aluminium. As basic phosphates of iron and aluminium are certainly forms of phosphoric acid which can be only slowly appropriated by plants, it is evident that the main effect of soluble phosphate must be yielded within a short time of its application.

The insoluble phosphate of superphosphate was formerly supposed to consist simply of the original phosphate of the material which had escaped the action of the acid; we now know that the insoluble phosphates consist partly, and in some superphosphates largely, of "reduced phosphates," which, we have already seen, are phosphates of iron and aluminium. The insoluble phosphates of superphosphates may be classed as—calcium phosphates less basic than tricalcic phosphate, unacted-on bone, precipitated phosphates of iron and aluminium, and unacted-on mineral phosphate. The manurial value of these various kinds of insoluble phosphate will doubtless stand in the order in which we have named them. It has been argued by some chemists that the manurial value of reduced phosphate must be equal to that of soluble phosphate, because soluble phosphate becomes itself reduced after contact with soil. We must recollect, however, that soluble phosphate is first dissolved and distributed through a considerable bulk of soil before reduction takes place. This facility of distribution is the main cause of the great value of soluble manures, and is entirely wanting in the case of ready-formed reduced phosphates. If only for this reason, reduced phosphate must have a far lower manurial value than soluble phosphate. Although the insoluble phosphate of superphosphate plainly consists of phosphates of different value, chemical analysis is unfortunately unable to distinguish satisfactorily between them, or to ascertain the quantity of each.

Besides soluble and insoluble phosphates, superphosphate contains a large amount of gypsum. The proportion of gypsum is of course greater where the phosphates have originally contained an excess of calcium, either as carbonate or fluoride. As this gypsum is in a very fine state of division, it forms an important constituent of the manure, and for some soils and crops adds considerably to its value.

The nitrogenous matter of turnip manure, and other mixed superphosphates, may also have very different manurial values. If the nitrogen exist in the form of ammonia or nitric acid, it will be in the highest degree available for the plant's use; if present as the animal matter of bone or blood, it will also be entirely, but more slowly, available as manure. If the nitrogen occur as woollen fibre (shoddy), it will, if the fibre exists entire, be more slowly available than the nitrogen of bone. Shoddy is, however, very completely disintegrated when mixed with sulphuric acid and a phosphate, and subjected to the heat of the manure pit. Shoddy also readily dissolves in hot chamber acid, and has sometimes been used in this state in the preparation of turnip manures. The changes which woollen fibre suffers by solution in sulphuric acid, or by contact with acid in the manure pit, are little understood, and it is impossible to say what may be the manurial value of the nitrogenous substances produced. According to Braconnot, the action of sulphuric acid on wool gives rise to a variety of nitrogenous products. By chemical analysis of a manure, the quantity of ready-formed ammonia and nitric acid can easily be ascertained. The quantity of nitrogen present in organic combinations is more difficult of estimation, and the particular source and actual condition of such nitrogen can very seldom be ascertained.

Gypsum is a manure supplying lime and sulphuric acid to the soil. The waste gypsum of tartaric acid works, and of candle factories, is commonly employed in the composition of manures. Native gypsum usually contains a small quantity of carbonate of calcium. As porous soils are continually losing sulphate of calcium by drainage, gypsum is on such soils a generally useful manure, though of limited effect. Crops such as clover and turnips, which contain much sulphur, are those most benefited by its application. We have already seen that superphosphate contains a large amount of gypsum; where

therefore superphosphate is used, applications of gypsum are unnecessary.

Lime, with *Chalk* and *Marl*, are manures largely used; the plant food which they supply is mainly limited to one element—lime; small quantities of phosphoric acid may, however, also be supplied. Lime prepared from dolomite will also furnish a considerable amount of magnesia. On soils naturally destitute of lime these manures are very valuable, as supplying the missing element; but in the majority of cases the beneficial influence of lime is due to its mechanical and chemical action within the soil. The addition of lime to clay soil effectually disintegrates the clay, and thus produces very beneficial results. The chemical effects of lime consist in promoting the oxidation of humus, and in liberating a portion of the combined potash and phosphoric acid of the soil; the quantity of available plant food within the soil being thus increased. The presence of lime is also essential to the exercise of the absorptive power of soils, at least as far as a large class of manurial constituents are concerned. Lime is also probably necessary for the assimilation by the plant of such salts as sulphate and chloride of ammonium. The best lime and chalk is that which breaks up most thoroughly on the land. The waste lime from the purifiers of gas works is on the whole of inferior value, and may be injurious if not first thoroughly exposed to air before use.

Potassium Salts.—The means at the farmer's disposal for restoring to the land the potash removed by sale of crops, or for enriching naturally poor soil with this element, were till within the last twelve or thirteen years very limited. The farmer had in most cases to rely on the importation of purchased food to be consumed by stock upon the land, or to employ small applications of vegetable ashes. The discovery of large beds of potassium salts at Stassfurt in Prussia, and at Leopoldshall in Anhalt, has happily placed moderately cheap potash manures at the farmer's disposal. The potash beds at Stassfurt and Leopoldshall are about 150 feet thick, and rest on the surface of an enormous deposit of rock salt. The native potassium salts are of very various composition, and contain much chloride and sulphate of magnesium, and common salt. From the crude salts Dr. FRANK succeeded in obtaining potassium salts of considerable purity. The general percentage composition of the potash manures at present prepared at Stassfurt is given by E. WOLFF as follows:—

TABLE IX.—AVERAGE PERCENTAGE COMPOSITION OF GERMAN POTASH SALTS.

	Potash Guaranteed.	Potassium Sulphate.	Potassium Chloride.	Magnesium Sulphate.	Magnesium Chloride and Magnesia.	Sodium Chloride.
Potash manure,	10—12	18—25	—	15—25	3—6	35—55
" concentrated,	25—26	22—26	19—22	15—20	3—6	20—35
" three times concentrated,	30—34	—	48—55	5—10	3—6	30—50
" four times concentrated	38—42	—	60—67	—	3—6	30—40
" five times concentrated	50—55	—	80—85	—	3—6	10—20
Crude potassium magnesium sulphate,	15—17	27—30	—	25—30	3—6	25—40
Leopoldshall (Anhalt) Kainit,	13—14	23—25	—	25—30	(?)	30—45

Kainit, and calcined kainit (the latter is called in the table "crude potassium magnesium sulphate"), are the potash manures most largely employed in this country. Kainit in its pure state has the composition $KCl + MgSO_4 + 3H_2O$, or, according to other chemists, the elements are arranged as $K_2SO_4 + MgSO_4 + MgCl_2 + 6H_2O$. Kainit should thus contain just 19 per cent. of potash. It is, however, very rarely found pure, being intimately associated with carnallite ($KCl + MgCl_2 + 6H_2O$), common salt, or chloride of magnesium; its composition is thus very various. Kainit is superior in quality the smaller the amount of chloride of magnesium present, the latter salt being very hygroscopic. Kainit is for the same reason improved by calcination, by which not only is water lost and the salt rendered more concentrated; but the chloride of magnesium is to some extent decomposed, and caustic magnesia formed. The Anhalt mines yield the largest amount of kainit.

Kainit is clearly a bulky manure, supplying only a very moderate amount of potash; large quantities of it cannot also be employed at once, as an excess of any soluble salt is injurious to plants. It produces its greatest effect when applied with superphosphate to light land; thus applied it sometimes produces considerable effects on pasture, and on leguminous and root crops.

Wood Ash is, where it can be obtained in quantity, an excellent potash manure. The ash of pine wood contains, according to WOLFF, about 6 per cent. of potash, and the ash of ordinary deciduous timber 10 per cent.; 4·5 to 6·5 per cent. of phosphoric acid is also present. The principal ingredient of wood ashes is carbonate of calcium. The ash of small boughs, twigs, and leaves is much richer in potash.

Common Salt.—This substance is occasionally employed as a manure. The ingredients it supplies—chlorine and sodium—are both of doubtful efficacy as plant food. Salt has, however, in some cases a beneficial effect from its action within the soil, by which small quantities of ammonia, potash, and other ingredients of plant food are liberated for the plant's use. Commercial salt, if tolerably free from insoluble impurities, is sufficiently good for all agricultural purposes.

We have now completed our description of the manures employed in agriculture. We treated, in the first place, of the exports of a farm, which necessitate the return to the land of the more important of the ingredients removed; we have now completed a review of the various imports, natural and artifi-

cial, by which in modern agriculture the fertility of the land is restored or raised to a point higher than before. We have next to inquire what principles should govern the use of these manures?

If a crop has just removed from the soil a certain quantity of nitrogen, phosphoric acid, potash, or other constituents, should the farmer at once endeavour to return the lost matter to the land? Or, when the farmer is desirous of preparing land for the growth of a particular crop, ought he to manure the soil with all the constituents of that crop, or at least with those constituents which it contains in preponderating quantity?

These two principles of restoration and manuring are those which naturally first occur to the scientific student of the subject; they have been put forward by clever theorists as being the only sound and rational principles of action; but, in fact, they are foreign to all good agricultural practice, would produce but inferior results if fully carried out, and in most cases would be attended with an expense that must always prevent their general adoption. Manuring, according to these principles, would lead us to apply an abundant dressing of silica for a wheat crop, to treat turnips with a heavy dressing of potassium salts, and to supply red clover and beans with twice as much nitrogen as would be given to wheat or barley. The principle of complete restoration would teach us to manure our clover leys with the immense amount of nitrogen removed in the crop, and scrupulously to return to our clay land the silica and potash furnished by it. Such modes of proceeding, we need hardly say, would be agricultural folly.

The true economical principle of manuring is *to supply the soil with the element or elements in which it is relatively deficient, in respect of the requirements of the crop it is intended to grow.* A good clay soil, for instance, or one derived from igneous rocks, is generally rich in available potash, and contains minerals which, by their decomposition, are continually yielding fresh supplies of that substance. To apply potassium salts to such a soil is practically to throw the manure away, as no return will be obtained from the expenditure. Where a soil is characteristically rich in any element of plant food, the supply of that element may clearly be dispensed with.

But not only does the character of economic manuring depend on the composition of the soil, it depends also on the requirements of the crop. What are the special food requirements of any crop cannot be determined from its composition, as we should at first naturally suppose; they can be ascertained only by a study of the crop during growth. It is, indeed, quite true that a crop must be supplied with *all* the ingredients which enter into its composition; but this truth is largely governed in practice by the fact that different orders of plants have very different capacities for obtaining food, and the more carefully crops are studied the more does this distinctive character of each appear. The luxuriance of a crop thus depends not merely on the quantity of food in the soil, but on its capacity for appropriating it. Every plant has strong and weak points in its powers of assimilation, and it is the part of a skilful husbandman to be acquainted with these, and to assist the plant with manure where it is naturally weakest.

It is easy to illustrate by examples the difference in the feeding powers of different crops. Leguminous plants are well able to supply themselves with nitrogen, and to attain a vigorous growth in soils which, unless artificially dressed with nitrogenous manure, would yield very poor crops of wheat or barley. Experience, again, has amply shown the efficacy of phosphatic manures for turnips, and the generally small effect of potash; yet the turnip crop really contains four or five times more potash than phosphoric acid. It is evident, therefore, that the turnip can appropriate the potash of the soil far more readily than the phosphoric acid, and an artificial supply of easily-assimilated phosphates becomes, in most cases, the economic manuring demanded by this crop. We may illustrate the same fact from the cereals. Cereal crops are the least nitrogenous of all the crops grown by the farmer, yet they stand in most need of artificial supplies of nitrogen. On soils yielding to analysis considerable quantities of nitrogen, wheat is frequently a very poor crop; while the application to this land of a small quantity of a soluble nitrogenous manure may at once double the produce. Cereals have, compared with other crops, little power of assimilating nitrogen; economic manuring clearly, therefore, requires that in their case the supply of available nitrogen should receive special attention.

The special manuring which we have just pointed out to be most consistent with economy is not attended with exhaustion of the soil, if a proper rotation is followed. Land which receives superphosphate for one crop, nitrate of sodium for a second, and farm-yard manure for a third or fourth crop, is not exhausted by this treatment; a complete manuring has been given; all the important constituents removed in the crops have been restored; but the manure has been distributed according to the special necessities of the individual crops, and has consequently yielded the most economical results.

Having made it evident that the special characters of a crop must be known if manure is to be economically applied, we cannot do better than present our readers with a brief account of the results yielded by Lawes' field experiments at Rothamsted, in Hertfordshire, which supply by far the best information we have on this part of our subject. The results obtained at Rothamsted will further serve to illustrate other very important facts belonging to the action of manures.

The soil at Rothamsted is a heavy loam containing flint; it rests on clay, with a chalk subsoil about 6 feet from the surface. The general plan of the field experiments is to grow the same crop year after year on the same land. The fields are divided into plots, each of which is constantly manured in the same manner. The whole of the produce is removed from the soil. By this mode of proceeding the per-

manent effect of each system of manuring becomes apparent, and exhaustion or accumulation is made evident; the effect of season is also shown, and trustworthy averages are obtained.

Wheat Experiments.—The first experimental crop of wheat was taken in 1844; since then the field has borne wheat every year. As the manuring was somewhat variable in the earlier years of the experiment, we will take for the purpose of average results the period of twenty years, 1852–71. The following table gives the average produce on some of the principal plots during this period:—

TABLE X.—AVERAGE PRODUCE OF WHEAT PER ACRE DURING TWENTY YEARS.

Plot Numbers.	Manures per Acre.	Dressed Corn.	Straw and Chaff.	Total Produce.	Corn to 100 Straw.	Weight per Bushel of Dressed Corn.
		Bushels.	Cwts.	Lbs.		Lbs.
3	Unmanured	14½	13	2 65	64·4	57½
1	Alkali salts	15⅛	13⅞	2507	61·9	58⅜
0	Superphosphate,	17¾	15¼	2819	66·5	58¾
5	Mixed cinereals,	17	15¼	2746	65·0	58⅞
10 *a*	Ammonium salts, 400 lbs.,	22½	21⅝	3865	58·9	57⅛
11	" 400 lbs., with superphosphate,	28	26⅝	47.6	60·4	57⅜
7	" 400 lbs., with mixed cinereals,	35¼	35⅞	6187	56·5	59½
9 *b*	Nitrate of sodium, 550 lbs.,	26⅛ *	28⅝ *	4819 *	52·5	56¾ *
9 *a*	" 550 lbs., with mixed cinereals,	38¾ †	47⅛ †	7325 †	50·1	59 †
2	Farm-yard manure, 14 tons,	35⅞	33⅛	6004	60·4	60

* Mean of nineteen years. † Mean of seventeen years.

The first point shown by the table is, that it is quite possible to grow good crops of wheat on the same land without intermission if suitable manure be applied. Wheat has now (1877) been grown for thirty-four seasons on this field, and on such plots as 7, 9*a*, and 2, good crops are always obtained if the season is a favourable one.

We learn further that purely inorganic manures, as the mixture applied to 9*a*, are all that is demanded for the nutriment of the crop. The produce of plot 9*a* exceeds, indeed, that of farm-yard manure on plot 2. Wheat is thus clearly capable of obtaining from the atmosphere all the carbon it requires, even when heavy crops are produced.

The above results show with equal plainness, that wheat is not capable of obtaining from the atmosphere a quantity of nitrogen sufficient to produce a full crop. That the whole supply of nitrogen from the atmosphere is inadequate for this purpose, is shown by the results on plot 5. The mixed cinereals applied to this plot consist of superphosphate of lime, and the sulphates of potassium, sodium, and magnesium; with the exception, therefore, of silica, all the important ash constituents of the crop are abundantly furnished, while no nitrogen is supplied. That an artificial supply of silica is not required by the wheat crop, is shown by the results on plots 7 and 9*a*, where good crops are produced without any silica being applied. The evidence on this point becomes still stronger when we recollect that the exhaustion of silica on these plots has been enormous, the whole of the produce being annually removed. The average produce on plot 5, by the manure supplying only the ash constituents of the wheat crop, is seen to be 17 bushels per acre; this amount is clearly a measure of the quantity of nitrogen obtained by the wheat crop from the atmosphere and soil under ordinary conditions of climate and tillage. The quantity of nitrogen thus assimilated from natural sources is about 22 lbs. per annum. When to this manure, supplying only the ash constituents of the wheat, nitrate of sodium or ammonium salts are added (plots 9*a* and 7), the produce is at once more than doubled; the nitrogen necessary for a full crop being thus artificially supplied.

These results are of great importance, as disproving LIEBIG's "mineral theory," a theory which was at one time widely held. In 1843 LIEBIG published the third edition of his "Organic Chemistry, in its Applications to Agriculture and Physiology." In this work he says—"Cultivated plants receive the same quantity of nitrogen from the atmosphere as trees, shrubs, and other wild plants; and this is quite sufficient for the purposes of agriculture." He further says—"Is fertility not quite independent of the ammonia conveyed to the soil? If we evaporated urine, dried and burned the solid excrements, and supplied to our land the salts of the urine and the ashes of the solid excrements, would not the cultivated plants grown on it—the *Gramineæ* and *Leguminosæ*—obtain their carbon and nitrogen from the same sources whence they are obtained by the *Gramineæ* and *Leguminosæ* of our meadows? There can scarcely be a doubt with regard to these questions, when we unite the information furnished by science to that supplied by the practice of agriculture." The question is summed up by saying—"The crops on a field diminish or increase in exact proportion to the diminution or increase of the mineral substances conveyed to it in manure." Baron LIEBIG here clearly maintained the uselessness of nitrogen or carbon as an ingredient of manures, and ascribed the increased produce resulting from manuring solely to the ash constituents which the manure supplied. It is also evident from a comparison of the last two quotations, and many others might be added, that by the term "mineral" he designated the ash constituents of plants, as opposed to the combustible nitrogenous and carbonaceous matters which they contain. The original mineral theory was amply disproved, both by the exact experiments at Rothamsted, and by general farm practice. It is sad to have to add that in later years LIEBIG, instead of acknowledging his mistake, asserted that by the term

"minerals" he included ammonia and nitric acid! The mineral theory of his later life was simply that the food of plants was purely inorganic, a statement the general truth of which no one disputes.

We have seen that the ash constituents of wheat yielded when applied alone but 17 bushels of grain; this was the measure of the nitrogen naturally available. On turning to plots 10*a* and 9*b*, we see the produce yielded by nitrogenous manures supplying none of the important ash constituents; the produce here is plainly a measure of the ash constituents naturally available. The much larger crops obtained on these plots than were obtained by supplying ash constituents only, proves that the natural supply of ash constituents in the soil was considerably more effective than the natural supply of nitrogen. This relation between the two is at the present date still very manifest on the experimental field, although the exhaustion of the soil of ash constituents on plots 10*a* and 9*b* has become enormous. Since 1844 plot 10*a* has received none of the ash constituents of the wheat crop, and the whole of the produce has been removed from the land. The soil of this plot has lost by thirty years' wheat cropping probably about 470 lbs. of phosphoric acid, and 680 lbs. of potash per acre: a loss of phosphoric acid which, according to Table III., would only occur in fifty-five years of ordinary rotation, and a loss of potash equivalent to one hundred and thirty-three years of the same rotation. Notwithstanding this exhaustion, which would never take place in actual practice, the available cinereal food in the soil still considerably exceeds the available nitrogenous food; and this will be found to hold true in the majority of cases in which cereal crops are cultivated, and consequently manuring with nitrogen will produce a far greater effect on these crops than manuring with cinereals.

It is seen by the table that on adding superphosphate to the ammonium salts the produce is raised $5\frac{1}{2}$ bushels, and by further adding salts of potassium, sodium, and magnesium, the produce is increased by another $7\frac{1}{4}$ bushels. Such an increase as this will very rarely be obtained in ordinary practice, the soil in the present case being far more exhausted of cinereal food than under the ordinary conditions of farming. It will, however, generally be found that a mixture of phosphates and nitrogen for cereal crops is decidedly more economical than a purely nitrogenous manuring. With regard to the large increase obtained by the use of alkali salts, we may mention, that in experiments not included in the table, potassium, sodium, and magnesium sulphate were *separately* employed, each of them in mixture with superphosphate and 400 lbs. of ammonium salts. The result in twenty years did not show that one of these salts was superior to the other. It would appear consequently that the wheat plant was excellently able to supply itself with potash, and that the effect of the alkali salts was simply to render the plant food of the soil more available. Common salt, as is well known, is occasionally applied to wheat with excellent effect. It probably brings into use the residues of previous manuring.

The experiments quoted in the table show the effect of nitrogen in three forms—as ammonia, nitric acid, and ordinary farm-yard manure. Supposing the ammonium salts and nitrate of sodium to contain 5 per cent. of impurities, the former (a mixture of equal parts chloride and sulphate) would supply 90 lbs. and the latter 86 lbs. of nitrogen. The farm-yard manure is estimated to contain 200 lbs. of nitrogen. It is evident from the relative weight of the crops, that the large quantity of nitrogenous matter in dung is really not so effective as the far smaller quantity supplied in the form of ammonia or nitric acid. The nitrogen in dung exists chiefly as organic compounds; these have to undergo oxidation in the soil before they can be assimilated by the plant. The action of dung is thus always slow, and is limited by the extent to which the soil is aerated.

Barley Experiments.—In Table XI. is given the average produce during twenty years (1852-71) of some of the more characteristic plots of the barley field:—

TABLE XI.—AVERAGE PRODUCE OF BARLEY PER ACRE DURING TWENTY YEARS.

Plot Numbers.	Manures per Acre.	Dressed Corn.	Straw and Chaff.	Total Produce.	Corn to 100 Straw.	Weight per Bushel of Dressed Corn.
		Bushels.	Cwts.	Lbs.		Lbs.
1 0	No manure,	20	$11\frac{1}{4}$	2454	86·6	52·3
3 0	Alkali salts,	$22\frac{3}{8}$	$12\frac{1}{4}$	2641	92·4	53·0
2 0	Superphosphate,	$25\frac{1}{2}$	$13\frac{3}{8}$	2931	97·1	53·2
4 0	Mixed cinereals,	$27\frac{3}{8}$	$14\frac{3}{8}$	3162	96·4	53·4
1 A	Ammonium salts, 200 lbs.,	$32\frac{1}{2}$	$18\frac{1}{2}$	3919	89·2	52·1
3 A	" 200 lbs., with alkali salts.	35	$20\frac{3}{4}$	4317	86·3	52·8
2 A	" 200 lbs., with superphosphate,	47	$27\frac{5}{8}$	5760	86·8	53·5
4 A	" 200 lbs., with mixed cinereals,	$46\frac{1}{4}$	$28\frac{1}{2}$	5817	83·2	54 0
1 C	Rape cake (mean, 1300 lbs.),	$45\frac{1}{4}$	$26\frac{7}{8}$	5571	87·3	53·8
7	Farm-yard manure, 14 tons,	$48\frac{1}{4}$	$28\frac{1}{4}$	5933	88·5	54·3

With barley, as with wheat, there is no difficulty in growing a continuous series of crops if suitable manure be applied. The sufficiency of inorganic food for a cereal crop, and the inadequate character of the atmospheric supply of nitrogen, are also shown as plainly in the barley experiments as in those with wheat. These points will not require fresh discussion.

It will be noticed that the addition of superphosphate to the ammonium salts (plot 2A) produces a much larger increase of crop than is the case with wheat; and that the further addition of alkali salts

(plot 4A) fails to increase the crop, although in the case of wheat the alkali salts were most effective. We should gather from these results, that the shorter-rooted and shorter-lived barley had rather less capacity than wheat for obtaining phosphates from the soil. That barley has a greater capacity than wheat for supplying itself with alkalies may be true, but can scarcely be proved, as the considerable effect of the alkalies on the wheat crop appears to be due to some secondary action. The barley plots manured with superphosphate are found to ripen one or two weeks earlier than the corresponding plots without superphosphate.

In the barley field nitrogen is applied as nitric acid, ammonia, rape cake, and farm-yard manure. As in the wheat field, the nitrogen in the form of nitric acid or ammonia is seen to be far more effective than the nitrogen of farm-yard manure. The rape cake was applied at the rate of 2000 lbs. per acre during the first six years, and at the rate of 1000 lbs. per acre afterwards: the cake supplied more nitrogen than either the ammonium salts or nitrate. The smaller dressing of 1000 lbs. of rape cake would contain about 48 lbs. of nitrogen, while 200 lbs. of ammonium salts would contain about 45 lbs.; 1000 lbs. of rape cake would also supply about 25 lbs. of phosphoric acid and 13 lbs. of potash. Owing to the presence of these important ash constituents, rape cake, when applied alone, gives a better return than either ammonium salts or nitrate of sodium; but when the ammonium salts or nitrate are mixed with superphosphate, they then produce a larger crop for the amount of nitrogen applied than is yielded by the rape cake, even when the latter is also mixed with superphosphate. Rape cake is an excellent manure, especially for light land. Its nitrogen is in the form of organic compounds, but is far more available than the nitrogen of farm-yard manure, being associated with far less carbonaceous matter, and thus more readily oxidised in the soil. Of all the nitrogenous manures applied to wheat and barley, nitrate of sodium is apparently the most effective.

A comparison of the results obtained with wheat and barley shows that barley yields a better return than wheat for the same amount of nitrogen applied. When ammonia is not employed in excess, and a sufficient amount of cinereal food is present, LAWES and GILBERT reckon that 5 lbs. of ammonia will on an average yield 1 bushel of wheat and its usual proportion of straw, and that $2\frac{1}{4}$ lbs. of ammonia will yield in the same way 1 bushel of barley. Or the same weight of total produce is obtained by the application of 14 lbs. of ammonia to wheat, and 9 lbs. to barley. In the experiments, however, from which these calculations were made, the ammonium salts are applied to wheat in the autumn and to barley in the spring; any loss of manure from winter drainage falls therefore upon the wheat, and not on the barley crop.

As barley yields a greater return for nitrogen applied than wheat, it follows that an amount of nitrogenous manure, not more than sufficient for a wheat crop, will be excessive for a barley crop grown under similar circumstances, and this is fully borne out by the Rothamsted experiments.

Further evidence of the greater capacity of barley for appropriating the nitrogen of the soil, is shown by the greater weight of produce which it yields with purely cinereal manures. The total produce of wheat with mixed cinereal manure was 2746 lbs.; with barley, 3162 lbs. per acre. The barley crop was not only heavier, but contained much more nitrogen. The unmanured barley, and the other barley plots receiving no nitrogen, have considerably fallen off in produce during the later years of the experiment, from the gradual exhaustion of the nitrogen of the soil.

Oat Experiments.—The experiments with oats (Black Tartarian) are on a more limited scale than those with wheat or barley. The average produce of five years (1869-73) is given in Table XII.

TABLE XII.—AVERAGE PRODUCE OF OATS DURING FIVE YEARS.

Plot Numbers.	Manures per Acre.	Dressed Corn.	Straw and Chaff.	Total Produce.	Corn to 100 Straw.	Weight per Bushel of Dressed Corn.
		Bushels.	Cwts.	Lbs.		Lbs.
1	No manure,	$19\frac{7}{8}$	$10\frac{1}{8}$	1988	72	$33\frac{3}{4}$
2	Mixed cinereals,	$24\frac{1}{2}$	$15\frac{1}{8}$	2532	70	35
3	Ammonium salts, 400 lbs.,	47	$28\frac{1}{2}$	5186	65	$35\frac{7}{8}$
4	Nitrate of sodium, 550 lbs.,	$47\frac{1}{8}$	$27\frac{3}{4}$	5110	69	$35\frac{1}{2}$
5	Ammonium salts, 400 lbs., with mixed cinereals,	59	$41\frac{1}{8}$	7160	58	37
6	Nitrate of sodium, 550 lbs., with mixed cinereals,	$57\frac{1}{2}$	35	6347	67	$35\frac{3}{4}$

The manures exhibit the same general results as in the wheat and barley experiments. The unmanured produce, and the produce with cinereal manure, is, however, distinctly smaller than with the other cereal crops. The crops with purely nitrogenous manures are large, only a limited exhaustion of the soil having as yet taken place.

LAWES and GILBERT have determined the proportion of nitrogen which is under various circumstances recovered in cereal crops for one hundred supplied in the manure; the experiments have been made with wheat, barley, and oats. In every case the crop was abundantly supplied with the necessary ash constituents, and the increase due to the nitrogenous manure was ascertained by subtracting from the produce yielded by the mixed nitrogenous and cinereal manure that given on other portions of the field by the cinereal manure alone. The results of the calculation are shown in Table XIII. The figures for wheat and barley are the average of twenty years' experiment; the figures for oats are the average of three years only, and are consequently less reliable.

TABLE XIII.—NITROGEN RECOVERED IN THE INCREASE FOR 100 SUPPLIED IN MANURE.

Manures per Acre.	Wheat.	Barley.	Oats.
Cinereals and ammonium salts (41 lbs. nitrogen),	32·4	48·1	—
" " (53·3 lbs. nitrogen),	—	49·8	—
" " (82 lbs. nitrogen),	32·9	—	51·9
" " (123 lbs. nitrogen),	31·5	—	—
" " (164 lbs. nitrogen),	28·5 *	—	—
" and sodium nitrate (82 lbs. nitrogen),	45·3	—	50·4
" and rape cake (61·75 lbs. nitrogen),	—	36·3	—
Farm-yard manure (about 200 lbs. nitrogen),	14·6	10·7	—

* Average of thirteen years.

The experiments with wheat are the most complete. We see that when the amount of ammonia applied to the land exceeds 82 lbs. of nitrogen (400 lbs. ammonium salts*) per acre, the proportion assimilated by the crop diminishes. The best result of all is obtained with nitrate of sodium, which being supplied as a top dressing in spring suffers no loss from winter drainage. Farm-yard manure is seen to yield a very low return for the amount of nitrogen which it contains.

Barley gives a better return for the nitrogen applied than wheat. The ammonium salts are always applied to the barley field in the spring, and would be expected, therefore, to yield a better crop than the autumn applications in the wheat field. The spring dressings of ammonia to barley are seen, however, to yield a greater return than even the spring dressings of nitrate to wheat, a clear proof of the greater assimilating powers of barley. In the case of farm-yard manure the figures show a less return of nitrogen in the barley than in the wheat crop; but the comparison is not a fair one, the wheat plot having received dung for nine years longer than the barley plot, and therefore possessing a greater accumulation of manure.

Oats apparently yield the best return for the nitrogen applied; but the experiment in this case is too brief for the result to be insisted on.

It is evident from the facts just quoted that cereal crops assimilate only a small part of the nitrogen supplied to them in manure. The unused nitrogen is partly accumulated in the soil, and partly lost by drainage, and possibly in other ways. The value of the nitrogen left in the soil for subsequent crops depends on the character of the manure from which it is derived, and the nature of the crop which follows it. The immense nitrogenous residues remaining from farm-yard manure have a very considerable and lasting effect on subsequent crops. This is shown at Rothamsted in experiments on barley, grass, and roots. Residues of rape cake have also a very distinct effect on following crops. The action of ammonium salts or nitrates is, however, almost confined to the first year of application. Experiments in the barley field show that large residues from previous dressings of ammonium salts and nitrate of sodium will produce a small increase in subsequent crops, the effect of the residues being spread over many years. In the wheat field much larger residues of ammonia have yielded only small and rapidly-diminishing results. On one plot in the wheat field as much as 800 lbs. of ammonium salts had been applied per acre for thirteen years, with a liberal cinereal manure: of the very large quantity of ammonium so applied only $28\frac{1}{2}$ per cent. was recovered in the crop. The annual application of ammonia was then stopped, and the plot left unmanured. The total produce obtained in seven subsequent years only exceeded by $37\frac{3}{8}$ bushels the produce of land which had been long cropped without ammonia. Of this $37\frac{3}{8}$ bushels, resulting from the residue of previous manuring, $19\frac{3}{4}$ bushels were obtained in the first year after stopping the manure; the effect in the following six years was thus extremely small. Wheat is apparently less capable of making use of nitrogenous residues than barley.

Analyses of the soils of the wheat field to a depth of 27 inches prove that a considerable amount of the unused nitrogen is stored up in the soil, but clearly in a condition little available for the wheat plant. A still larger amount of the nitrogen applied has, however, disappeared; the greater part of this has apparently been washed into the subsoil in the form of nitrates.

The wheat field is tile-drained, each drain passing under the middle of a plot; the drain water has been from time to time collected and analyzed. The winter drain water from the plots receiving ammonium salts in the autumn generally contains more than 1 part of nitrogen in 100,000; the nitrogen (as nitrates) in the drain water being greatest where most ammonia has been applied. In one instance the nitrogen present reached 7·84 per 100,000. The late spring and summer drainage contains only a trace of nitrates. The drain water from the plots manured with nitrate of sodium is richest in nitrogen in the spring, shortly after the application of the manure. In one instance the amount of nitrogen in the drain water from these plots reached 5·38 per 100,000. It is evident from these results that the ammonium salts applied to a soil are quickly converted into nitrates, and that large quantities of nitrogen may be lost by the washing out of these nitrates in heavy rains. LAWES and GILBERT calculate that if the drain water contains 1 part of nitrogen in 100,000, there will be a loss of 2·26 lbs. of nitrogen per acre for every inch of rain that

* LAWES and GILBERT assume that 400 lbs. of ammonium salts, and 550 lbs. of nitrate of sodium, will each supply about 82 lbs. of nitrogen; the amount really supplied is, perhaps, rather more.

passes below the range of the roots. The drain gauges at Rothamsted show that one-third of the rainfall may pass below a depth of 40 inches; this will chiefly occur in winter, when there is little evaporation from the surface. The practical lesson from these valuable investigations is clearly that soluble nitrogenous manures should not be applied to land until the crop is ready to appropriate them.

From the plot receiving farm-yard manure every year very little drain water ever runs, the soil having become porous and capable of holding much water; the drain water when collected contains comparatively but little nitrate. On this plot there is apparently a considerable loss of nitrogen which cannot be accounted for by drainage. It seems likely that, in the decomposition of the organic matter in the presence of only a limited amount of oxygen, a part of the nitrogen has been evolved in the form of nitrogen gas.

Cinereal manures are, like nitrogenous manures, only partly appropriated by growing crops. The effect of the residues of cinereal manures upon subsequent wheat crops has been studied at Rothamsted. There is no doubt that residues of superphosphate and alkalies are not nearly so effective as fresh applications of these manures; but such residues are certainly capable of producing a much greater effect than corresponding residues of ammonia or nitrates. There is practically no loss of the phosphates, and but little of the potash, applied to a fertile soil; the part unused by the crop remains stored in the upper layers of the soil. HERMANN VON LIEBIG has examined the wheat soils of Rothamsted after twenty-two years' application of manure. He found the accumulation of the phosphoric acid and potash to be chiefly in the first 9 inches of surface soil; none had apparently passed below the second 9 inches.

Pasture Experiments.—We may now leave the cereals, and pass to the experiments on permanent pasture. These experiments were commenced in 1856 in Rothamsted Park, and have now (1877) reached their twenty-second season. Table XIV. shows the average quantity of hay yielded by the more important plots during twenty years; the figures refer solely to the summer cutting, the autumn growth being fed off on the land, or otherwise returned to it.

TABLE XIV.—AVERAGE PRODUCE OF HAY DURING TWENTY YEARS.

Plot Numbers.	Manures per Acre.	Hay.
		Cwts.
3	No manure	21¼
4–1	Superphosphate	22¼
7	Mixed cinereals	35¼
5	Ammonium salts, 400 lbs.	26¼
4–2	Ammonium salts, 400 lbs., with superphosphate	32¼
9	Ammonium salts, 400 lbs., with mixed cinereals	51
15	Nitrate of sodium, 550 lbs.	35⅜ *
14	Nitrate of sodium, 550 lbs., with mixed cinereals	57 *

* Average of eighteen years.

The results obtained in these experiments with permanent pasture cannot be quite so simply interpreted as those of the crops already considered, from the fact that the herbage of a pasture is of a mixed character, and contains many species of plants which are differently acted on by manure. To such an extent has the growth of certain classes, and even certain species of plants, been affected by the character of the manuring, that the appearance of the various plots became wholly different shortly after the commencement of the experiments. In one plot clover became abundant, in others it entirely disappeared; certain free growing grasses and weeds also became characteristic of special plots. To investigate this influence of manures on the character as well as on the amount of the herbage, Messrs. LAWES and GILBERT have instituted periodical botanical analyses, in which the number of species on each plot, and the proportion of each to the total herbage, is carefully ascertained. The average results obtained in the botanical analyses of 1862, 1867, and 1872 for three plots, will sufficiently illustrate the subject for our present purpose.

TABLE XV.—AVERAGE NUMBER OF SPECIES, AND PERCENTAGE BOTANICAL COMPOSITION OF HAY VARIOUSLY MANURED.

	No Manure.		Mixed Cinereals.		Ammonia and Cinereals. *	
	Number of Species.	Percentage Composition of Hay.	Number of Species.	Percentage Composition of Hay.	Number of Species.	Percentage Composition of Hay.
Graminaceous herbage	17	66·66	17	57·59	13	94·11
Leguminous herbage	4	8·27	4	25·72	1	·01
Miscellaneous herbage,	27	25·08	21	16·69	7	5·88
Total,	48	100·00	42	100·00	21	100·00

* On this plot 800 lbs. of ammonium salts are applied per acre.

We see that manuring diminishes the number of species growing on a pasture, the plants which profit most by the manuring choking by their vigorous growth the more delicate species. The mixed cinereal manure which supplies no nitrogen is seen to favour to a remarkable degree the growth of clovers. Indeed, in 1872 the leguminous herbage on this plot amounted to 39·8 per cent. of the whole produce. This development of clover is plainly associated with the presence of potash in the manure; for on another plot, where only the potassium salts are omitted, the clover is quite small in quantity. Nitrogenous manures of all kinds favour the growth of the grasses, and exterminate other kinds of herbage. With liberal

dressings of ammonium salts clover is practically destroyed, even when the manure supplies an abundance of potash. We must therefore remember, in discussing the produce by various manures, that the crops obtained from the nitrogenous manures are almost purely graminaceous, while that yielded by the mixed cinereal manure is largely leguminous.

The application of superphosphate alone to the park land is seen to increase the produce but very little. The addition of alkali salts to the superphosphate largely increases the crop, though no nitrogen is applied. The increase includes both clover and grass.

Ammonium salts alone yield a very poor crop. The roots of grass are, in fact, shorter than those of wheat or barley, and are thus much less capable of collecting the required ash constituents from the soil. Nitrate of sodium applied alone yields a far better result than ammonium salts. The nitrate has apparently developed the growth of deeply-rooted grasses; these are of course better able to collect the cinereal food of the soil. From apparently the same cause the nitrate plots are found to suffer much less from drought than those receiving ammonia. One reason of the ill effects of ammonium salts, when applied alone for many years, is probably due to the great loss of lime which the surface soil suffers. As the plant assimilates ammonia only, the acid of the ammonium salt must combine with the carbonate of calcium of the soil, forming soluble compounds, which are washed into the subsoil. Not only is the surface soil thus deprived of the lime required as plant food, but it must also be recollected that in the absence of carbonate of calcium, ammonia, if combined with acids, becomes less effective as a manure. The application of nitrate of sodium will not, like ammonium salts, occasion a loss of lime, nor will it, like them, produce an acid condition of the soil. The nitrate of sodium will, in fact, leave a residue of carbonate of sodium in the soil, the plant assimilating more nitric acid than sodium. The carbonate of sodium thus left in the soil is probably efficacious in setting free the cinereal food which the soil contains.

The addition of superphosphate to ammonium salts decidedly increases the crop of hay, but the produce even then does not equal that of nitrate of sodium employed alone. The further addition of alkali salts to the ammonia and superphosphate has a much greater effect, and largely increases the produce of hay. Meadow hay is a crop containing much more potash than crops of wheat or other cereals; and since it has far shorter roots to collect potash with, it is not surprising that potash manures should produce a considerable effect on exhausted pasture. Nitrate of sodium, with mixed cinereals, is seen to give a somewhat better result than the corresponding plot receiving ammonia.

There are among the park experiments several of great interest which we have not described; enough has, however, been said to show the general character of a hay crop. If grass is continually mown for hay, care must evidently be taken to supply the land with the lime and potash which the crop requires, and which it is less capable of obtaining for itself than any other crop on the farm. Farm-yard manure furnishes the natural means of restoring the potash removed in the crop. Wood ashes may also be used with great advantage. We have seen that with purely cinereal manures the clover of the pasture is considerably developed; maximum crops of hay are, however, only obtained by the united use of nitrogenous manures with cinereals.

Bean Experiments.—We turn next to the Rothamsted experiments with leguminous crops, and first of beans. The field experiments with beans were commenced in 1847. The crops, after a few years, considerably diminished; in consequence of this, and of the foulness of the land, the first series of experiments concluded in 1859. The following table shows the average results on three of the principal plots during twelve seasons (1847–58):—

TABLE XVI.—AVERAGE PRODUCE OF BEANS PER ACRE DURING TWELVE YEARS.

No.	Manures per Acre.	Dressed Corn.	Total Straw.	Total Produce.	Corn to 100 Straw.
		Bushels.	Cwts.	Lbs.	
1	No manure, ...	15½	9⅜	2073	96·8
2	Superphosphate, ...	14⅞	9½	2016	88·7
3	Mixed cinereals, ...	21¾	12	2792	106·5

The figures in the table show that no increase of crop was obtained by the use of superphosphate alone, but that on adding salts of potassium, sodium, and magnesium to the superphosphate a considerably greater produce followed. We have just seen the striking effect produced by potassium salts in developing the growth of clover on pasture land. Potassium salts seem, indeed, to be especially effective for all leguminous crops. We shall see presently the same fact illustrated in the experiments with red clover.

The results obtained by applying ammoniacal manures to beans are shown in the following table, which gives the average amount of the crops during the first five years, 1847-51, after which the application of ammonia was stopped:—

TABLE XVII.—AVERAGE PRODUCE OF BEANS PER ACRE DURING FIVE YEARS.

No.	Manures per Acre.	Dressed Corn.	Total Straw.
		Bushels.	Cwts.
1	No manure, ...	25¼	14⅜
2	Superphosphate, ...	23⅞	14⅝
3	Mixed cinereals, ...	31¼	18
4	Ammonium salts, 200 lbs., ...	24⅜	14½
5	Ammonium salts, 200 lbs., with superphosphate, ...	27⅜	15⅛
6	Ammonium salts, 200 lbs., with mixed cinereals, ...	33⅞	19

With ammonium salts alone the produce is not greater than on the unmanured plot; and ammonium salts mixed with cinereal manures produce scarcely a larger crop than the cinereal manures applied alone. Ammonia is, indeed, practically without

effect, a result in striking contrast with the facts observed in the case of the cereals and grasses.

In 1860 the bean field was fallowed, and a crop of wheat afterwards taken; the experiments with beans were then resumed, nitrate of sodium being employed in place of ammonium salts. The results were similar to those previously obtained. The mixed cinereal manure produced a relatively greater effect owing to the increased exhaustion of the unmanured land. The nitrate was decidedly more beneficial than the ammonium salts, but the increase obtained by its use was irregular. All the combinations of manures tried failed to maintain a crop of tolerable amount.

The character of the bean crop is seen to be very different from that of the crops hitherto considered. Its indifference to nitrogenous manures; the considerable increase obtained by supplying ash constituents only; and the fact that the crop cannot be indefinitely repeated with success on the same land, even with ample manuring—are all points in which it greatly differs from the cereals and grasses, but in which it agrees with clover and other crops belonging to the order *Leguminosæ*.

The indifference of leguminous crops to nitrogenous manures becomes the more remarkable when we remember the large amount of nitrogen which enters into their composition. The small crop of beans yielded by purely cinereal manure (plot 3) must have contained during twelve years an average of 71 lbs. of nitrogen, a quantity equivalent to a wheat crop of 47 bushels. Yet this amount of nitrogen was annually obtained by the bean plants from the soil or atmosphere, without any supply of nitrogen in the manure.

Clover Experiments.—The first experimental crop of red clover was taken in 1849; it was followed by a crop of wheat unmanured. A second clover crop was taken in 1851. Since this time no considerable crop of clover has been obtained from the land, though it has been repeatedly sown, and various kinds of manure have been tried. The amount of the first and second year's crop on some of the principal plots is shown in Table XVIII.

TABLE XVIII.—PRODUCE OF RED CLOVER PER ACRE.

No.	Manures per Acre.	Hay, 1849.	Hay, 1851.
		Cwts.	Cwts.
1	No manure,	7·$\frac{1}{8}$	8$\frac{1}{4}$
2	Superphosphate, 2$\frac{1}{2}$ cwts.	79$\frac{3}{4}$	5$\frac{1}{4}$
3	Sulphate of potassium, 300 lbs.	97$\frac{1}{2}$	11$\frac{1}{4}$
4	Mixed cinereals,	92$\frac{3}{4}$	22$\frac{3}{4}$
5	Ammonium salts, 200 lbs.,	7·$\frac{1}{2}$	—
6	Ammonium salts, 200 lbs., with superphosphate,	78	—
7	Ammonium salts, 200 lbs., with mixed cinereals,	92	—

We have here a repetition of the results obtained with beans. Superphosphate has practically no effect when applied alone, but the addition of alkali-salts to the superphosphate (plot 4) gives a considerable increase. That this increase is due to the potassium salts contained in the alkalies is shown by plot 3, where sulphate of potassium is applied alone; this plot yielded in the first year the largest crop in the field.

Ammonium salts give no increase whatever, the crops obtained where ammonia is applied being practically the same as those yielded by corresponding plots receiving no ammonia. The indifference of the clover to nitrogenous manures is still more striking than in the case of beans, as the quantity of nitrogen demanded by such large crops of clover is enormous. The crops grown on plots 3 and 4 in 1849 must have contained about 250 lbs. of nitrogen per acre.

The fact that land becomes "clover sick" by the repeated growth of the crop is well known, and is abundantly illustrated by the failure of the field experiments at Rothamsted. Messrs. Lawes and Gilbert have tried to remedy the clover sickness of their experimental land by the application of all kinds of manures, in some cases mixed with the soil to the depth of 3 feet, but without substantial success. They sum up their experience by saying: "The general result of the experiments in the field has been, that neither organic matter, rich in carbon as well as other constituents, nor ammonia salts, nor nitrate of soda, nor mineral constituents, nor a complex mixture, supplied as manure, availed to restore the clover-yielding capabilities of the land; though where some of these (potash and nitrates) were applied in large quantity, and at considerable depths, the result was better than when they were used in only moderate quantities, and applied only on the surface."

There is one more experiment at Rothamsted with red clover; it is full of interest. In 1854 clover was sown in an old kitchen garden, the soil of which had been under cultivation for two or three centuries. The bed thus planted has for twenty-four seasons never failed to yield a crop, and the clover at present growing is still very luxuriant. During the twenty-four years clover seed has been applied five or six times to renovate the plant.

It is quite evident from these facts that where the character of the soil is suitable clover sickness does not exist. On what the favourable character of the soil depends, which renders it suitable for the continuous growth of clover, we have at present no certain information.

Root Experiments.—These field experiments were commenced in 1843. For the first six seasons (1843–48) Norfolk white turnips were grown; then swedes for four seasons (1849–52). After this barley was grown for three years. The experiments with swedes were then resumed, and continued for fifteen seasons (1856–70). From 1871 to 1875 the crop was sugar beet.

As root crops when removed from the land are extremely exhausting in their effects, we must consider separately the action of the manures in the early and later years of the experiments. In Table XIX. is shown the average crop on a few plots in the first two seasons (1843–44).

TABLE XIX.—AVERAGE PRODUCE OF WHITE TURNIPS DURING TWO YEARS, 1843–44.

Manures per Acre.	Roots per Acre.
	Cwts.
No manure,	64
Superphosphate, 5 cwts.,	199
Farmyard manure, 12 tons,	202¼

In the first year the produce by superphosphate was greater than that by farm-yard manure, in the next year it was below it, but on an average of the first two years it is about equal to it. After this period the produce by superphosphate was very much below that given by farm-yard manure.

We will next take the average of the last two years (1847–48) of the growth of white turnips. By this time a regular system of manuring had been adopted.

TABLE XX.—AVERAGE PRODUCE OF WHITE TURNIPS DURING TWO YEARS, 1847–48.

Manures per Acre.	Root.	Leaf.	Leaf to 100 Root.
	Cwts.	Cwts.	
No manure,	36	25	69
Ammonium salts, 200 lbs.,	40	20	50
Ammonium salts, 200 lbs.; rape cake, 2000 lbs.,	165	118	72
Superphosphate, 2½ cwts.,	160	49	31
" with ammonium salts, 200 lbs.,	208	93	45
" " with rape cake, 2000 lbs.,	228	158	69
Superphosphate, 2½ cwts., with alkali salts,	165	48	29
" with ammonium salts, 200 lbs.,	240	81	34
" " with rape cake, 2000 lbs.,	264	150	57

We see here that the unmanured produce had become in four years extremely small, and that superphosphate when used alone still continued to produce a large increase in the crop. A purely nitrogenous manure, as ammonium salts, has clearly very little effect; but when ammonia is added to superphosphate its action is seen to be decidedly beneficial. The rape cake supplied more than twice as much nitrogen as the ammonia, and also a rather considerable quantity of phosphoric acid. Salts of potassium, sodium, and magnesium have little effect, except on plots where the crops have been considerable, and the exhaustion of alkalies therefore large.

A further point of interest in the table is, that the proportion of leaf to root increases greatly with the quantity of nitrogen in the manure. A turnip in its earlier stages of growth produces chiefly leaf; when the development of the root actively sets in the leaf not only relatively but actually diminishes, the matter of the leaf being to a considerable extent absorbed, and passing into the root. A turnip with a large proportion of leaf is thus an immature turnip. We learn, therefore, from the table, what is well known in practice, that superphosphate applied alone brings turnips to an early state of maturity; while the addition of guano, or other nitrogenous manure, tends to prolong the period of growth. It will be observed that where alkali salts form part of the manure the proportion of leaf is reduced; the common practice of applying common salt to mangels is attended with a similar result.

We will now give some of the results obtained with swedes in a later stage of the experiment. Table XXI. shows the average of thirteen crops of swedes, 1856–70, two crops in this period failing.

TABLE XXI.—AVERAGE PRODUCE OF SWEDES PER ACRE DURING THIRTEEN SEASONS.

No.		Root.	Leaf.	Leaf to 100 Root.
		Cwts.	Cwts.	
1	No manure,	12	3	25·0
2	Nitrate of sodium, 550 lbs.,	22	5	22·7
3	Ammonium salts, 400 lbs.,	15	3	20·0
4	Ammonium salts, 400 lbs.; rape cake, 2000 lbs.,	76	16	21·1
5	Farm-yard manure, 14 tons,	144	19	13·2
6	Superphosphate, 3 cwts.,	60	10	16·7
7	" with nitrate of sodium, 550 lbs.,	108	20	18·5
8	" with ammonium salts, 400 lbs.,	87	17	19·5
9	" " with rape cake, 2000 lbs.,	134	31	23·1

The very small result obtained on the continuously unmanured plot is seen to be but little improved by the application of large quantities of purely nitrogenous manures. Nitrate of sodium (plot 2) is seen, however, to be superior in its effects to ammonium salts (plot 3).

Superphosphate continuously applied without any other manure is seen to give, even on this greatly exhausted land, a very considerable increase of crop, far exceeding that produced by purely nitrogenous manures. The addition of nitrogen to the superphosphate, however, considerably increases the produce; nitrate of sodium being clearly more effective than salts of ammonium. As in the experiments with turnips, we see that in proportion as the nitrogen added to the superphosphate is increased, so the

proportion of leaf to root also becomes greater; this is shown by a comparison of plots 6, 8, and 9. The evidence is not so striking as with turnips, the natural proportion of leaf in swedes being far smaller.

The character of the turnip crop, as to its capacity for supplying itself with food, is pretty clearly shown by the above long-continued field experiments. The crops, it is true, are very small even where farm-yard dung was continuously applied; this is probably due to the heavy character of the Rothamsted land, which requires to be lightened by the roots and stubble of cereal crops to preserve a favourable condition for turnips. The smallness of the crops will not, however, interfere with the interpretation of the results.

The weakest point in the turnip's feeding capacity is clearly its faculty for appropriating the phosphoric acid of the soil. As soon as the soil has become partially exhausted, nitrogenous manures produce hardly any effect unless accompanied by phosphates; while phosphates applied alone are capable of largely increasing the produce. It has been supposed by some that the effect of superphosphate on the turnip crop is mainly due to the sulphate of calcium which it contains. It is, indeed, probable that sulphates have a special value for the turnip crop, seeing that sulphur enters rather largely into its constitution; but as superphosphate made with hydrochloric, instead of sulphuric acid, has been found at Rothamsted to be an effective manure, and the sulphates of calcium and ammonium applied alone to have little influence, there is no reason to doubt that the action of superphosphate is really due to the phosphoric acid present.

It would appear that with respect to potash turnips are well able to supply themselves out of the natural resources of the soil, manuring with alkali salts, unless under very exhausted conditions of soil, producing little effect. Recent field experiments made in various parts of England have also shown that potassium salts do not increase the crop, except on very light poor land. We must remark once more in passing, how strikingly different this actual independence of artificial supplies of potash, and dependence on artificial supplies of phosphates, is from the idea which would be formed, *a priori*, from the composition of the turnip crop. Since both turnips and swedes contain about four times as much potash as phosphoric acid, we should naturally imagine that the former, rather than the latter, would prove most effective as an artificial manure.

The behaviour of the turnip crop towards nitrogen is full of interest. It is evident from the experiments now quoted, and from several others conducted at Rothamsted, that the turnip has a great power of appropriating the nitrogen of the soil. This is shown by the great and continued effect of superphosphate applied alone, in which case the whole of the nitrogen must clearly be derived from natural sources. It is shown also by the exhausted state, as regards nitrogen, in which the soil is left when turnips are removed from the land. After the first ten crops of roots, barley, as already mentioned, was grown for three years on the experimental land. On the part of the field where turnips had been grown with superphosphate only, the barley crop was far smaller than that yielded in the experimental barley field, where barley had been grown year after year without manure. Barley, in fact, exhausts the nitrogen of the soil much less speedily than turnips. The first ten crops of turnips, manured with superphosphate and alkalies, would remove from the land on an average at least 42 lbs. of nitrogen per annum; this is nearly double the quantity which would be contained in a similarly manured wheat or barley crop. In consequence of this exhausting character of the turnip crop, the yield of roots will rapidly diminish if they are grown year after year on the same land without the application of suitable manure.

We turn to the experiments with sugar beet. Table XXII. shows the average produce of root and leaf during three years (1871–73). In these three years the arrangement of the plots, and the manures applied, were the same as in the swede experiments last quoted.

TABLE XXII.—AVERAGE PRODUCE OF SUGAR BEET PER ACRE DURING THREE YEARS.

Plot Numbers.	Manures per Acre.	Root.	Leaf.	Leaf to 100 Root.
		Cwts	Cwts.	
3	No manure,	137	35	26
3 *a*	ammonium salts, 400 lbs.,	264	88	33
3 *n*	Nitrate of sodium, 550 lbs.,	385	122	32
5	Superphosphate, 3½ cwts.,	118	29	25
5 *a*	" with ammonium salts, 400 lbs.,	270	90	33
5 *n*	" with nitrate of sodium, 550 lbs.,	391	104	27
4	Superphosphate and alkali salts,	129	29	22
4 *a*	" with ammonium salts, 400 lbs.,	303	67	22
4 *n*	" with nitrate of sodium, 550 lbs.,	395	113	29

With sugar beet we come to a new species of plant, the chemistry of which is in some respects quite different from that of the turnip or swede. The first point that strikes one in the table is the very large crop of beet which is produced by purely nitrogenous manures, and especially by nitrate of sodium; whereas in the preceding experiments with swedes on the same land, a very small increase was obtained by such manuring. We next observe that superphosphate has in no case had any marked effect in increasing the crop, a result wholly different from what appears in the case of turnips. These two striking features of the experiment—the large effect produced by purely nitrogenous manure, and the

little result from applications of phosphate—are quite in harmony. The beet-root was clearly well able to supply itself from the soil with all the phosphoric acid it required; its roots are capable of attacking the combined phosphoric acid of the soil in a manner the turnip plant is unable to accomplish. The beet being thus sufficiently provided with cinereal food from the soil, the sole application of nitrate of sodium was quite enough to produce a large crop of roots.

Beet-root is perhaps as indifferent to manures supplying alkalies as the turnip crop; but on certain plots of the field, where the exhaustion of alkalies has been very great, a considerable increase is produced by the application of potassium salts, or of the usual mixture of alkali salts and magnesia.

Mangel-wurzel is merely a variety of beet-root, and will therefore be similarly influenced by manures. The usual practice of manuring mangel heavily with nitrogenous manures illustrates the facts shown in the Rothamsted experiments.

We have now described those of the field experiments at Rothamsted which display the special characters of the ordinary farm crops, and teach the principles on which their economic manuring should be based. There is one other point which we must briefly touch before leaving this part of our subject; this is the character of the residues left on the field by various crops, and the influence of these residues on the condition of the land.

The residue left on the land by a preceding crop consists of roots, or of roots and stubble. This residue is more considerable in proportion as the roots are of greater extent; and its value greatly depends on the composition of the roots, which is generally analogous to that of the plant to which they belong. Crops such as turnips, mangel, &c., leave very little residue in the soil, their rootlets being small, and in the case of the turnip confined to the surface. The residues of clover, and of other long-lived and deeply-rooted crops, may, on the other hand, be enormous.

Weiske and Werner determined in 1869 the amount and composition of the various residues left in the soil by the crops grown on the experimental station at Proskau. The soil after harvest was dug on measured plots to the depth of 10 inches; the roots and stubble were freed from soil by washing on a fine sieve, and were then dried and analyzed. The results are shown in Table XXIII.

TABLE XXIII.—STUBBLE AND ROOTS REMAINING AFTER HARVEST (POUNDS PER ACRE).

	Total Dry Substance.	Organic Substance.	Ash.	Nitrogen.	Lime.	Magnesia.	Potash.	Phosphoric Acid.	Sulphuric Acid.
Lucerne,	9702	8498	1204	137	197	25	37	40	19
Red clover,	8953	7026	1927	193	263	50	82	75	26
Sainfoin,	5952	4925	1027	124	118	32	43	30	21
Kidney vetch,	5023	4044	979	103	137	18	26	24	14
Serradilla,	3141	2594	547	65	80	14	9	19	9
Lupine	3547	2994	553	63	81	12	17	14	7
Peas,	3234	2560	674	57	72	11	11	15	10
Buck wheat,	2203	1736	467	48	81	7	9	11	7
Rye,	5283	3630	1653	66	74	15	32	26	12
Wheat,	3490	2396	1094	24	77	10	19	12	8
Oats,	3792	2343	1449	27	86	12	25	30	9
Barley,	1999	1617	382	23	43	6	10	12	6
Rape,	4475	3850	625	61	124	13	47	32	31

The total ash here given is in all cases too high, the ash being largely contaminated with fine sand, which it was found impossible to remove from the roots.

The results in this table must not be taken as having the value of averages, they are the result of a single season; they are, nevertheless, full of interest. We would point first to the immense residues left by the leguminous fodder crops, reaching in the case of lucerne to nearly 4 tons of dry organic matter per acre. In contrast with this we have the small residues left by wheat and oats, and especially by the more delicately-rooted barley. Not only are the residues of the leguminous fodder crops considerable, they are also very rich in nitrogen; the residue from red clover contains indeed nearly 200 lbs. of nitrogen per acre. The smaller residues of leguminous corn crops, as peas and lupines, are also seen to be relatively rich in nitrogen.

We have here an explanat on of the fact, so well known to farmers, that leguminous crops, and especially clover, are an excellent preparation for a cereal crop; a crop of wheat, indeed, following clover stands in no need of manure. At Rothamsted an unmanured field was sown, half with clover and half with barley; the following year barley was taken over the whole field without manure. The crops obtained were as under:—

First Half of Field.		Second Half of Field.	
1873 Barley,	31 bushels.	1873 Clover hay,	54 cwts.
1874 "	32¾ "	1874 Barley,	58 bushels.

The clover crop removed from the land an immense quantity of nitrogen; but it left accumulated at the surface, in the form of roots and stubble, an ample supply of food for a luxuriant crop of barley. There can be no doubt that the long-rooted leguminous fodder crops are of great use in bringing to the surface, and rendering available for other crops, the nitrogen which, in the form of nitrates, had passed by drainage into the subsoil. It is very doubtful, however, whether this explanation is sufficient to account for the great accumulation of nitrogen, both in the crop and in the surface soil, which occurs in the growth of clover.

We cannot now pursue the subject of crops further, nor have we space to consider the influence which manures have on the composition as well as

on the amount of the produce; we will conclude our consideration of the relation of manures to crops by a few general remarks.

It must always be borne in mind that in order to produce a given increase of crop, the quantity of manure used must always be considerably in excess of the amount which will be assimilated by the plant. One reason for this is, that it is impossible that all of the manure employed should come into contact with the roots. Such a result, so desirable on the score of economy, will, however, be favoured by employing soluble manures, or manures in a fine state of division, and by taking pains to insure their thorough mixture with the soil. Sowing a part of the manure by drill, so as to concentrate it near the seed, is also in many cases attended with economy. A water drill is specially suitable for such a purpose. In the case of a light sandy or gravelly soil, of little retentive power, the farmer is obliged to use soluble manures with great judgment; and bulky organic manures, as farm yard manure, rape cake, and bones, with the ploughing in of green crops, are the most certain means of improving the land.

As a considerable part of the manure applied is not, under the most favourable circumstances, taken up by the first crop, a more or less valuable residue of the manure will always remain in the land. Since all nitrogenous matter in the soil is gradually oxidised, and passes away in the drainage water as nitric acid, it is economical in most cases to keep the land as far as possible always under a crop, in order that the soluble nitrates may be utilized as soon as formed.

The continual accumulation of valuable residues in the land raises the condition of the soil. High condition is a state of great value. It means a thorough distribution of plant food throughout the soil, so that a crop has the best possible opportunity for vigorous growth, and is, as far as may be, independent of season. With high condition, however, often comes a waste of manure, the farmer still continuing to apply manure, which from the richness of the land produces no remunerative result. This is less likely to happen where a special manuring suitable to the character of each crop is followed, than where a general manuring, by feeding large quantities of artificial food, is adopted. The farmer can always, by small comparative trials in the field, ascertain for himself if a certain application of manure is profitable on his own land. Small field experiments of this nature will be most useful to the individual farmer; but their results must be very cautiously, if at all, applied to other farms, as the results obtained plainly depend on the condition of the soil, which on different farms may be very diverse.

Chemical Analysis of Manures.—This is the last division of our subject. The value of a manure plainly depends on the amount of plant food which it contains, and on the condition in which this food occurs; these points are more or less capable of being determined by chemical analysis. It will be quite impossible to describe the methods of analysis suitable for all the manures already noticed; we must limit our attention to the determination of the three most important elements of manure—nitrogen, phosphoric acid, and potash.

Preparation of Sample.—The first step in every analysis is the preparation of the sample. To prepare a fine powder which shall exactly represent the main bulk of the manure is no easy task, and demands much patience and judgment. A preliminary sample should first be made, by taking portions from many parts of the bulk; all large pieces should then be broken, and the whole well mixed. Where it is possible, after a rough mixing by hand or with a shovel, the whole should be passed through a coarse sieve. A sample is then taken for use in the laboratory from various parts of the rough mixture thus obtained. Mineral phosphates should, whenever possible, be ground to a fine powder between a clean pair of millstones, and small samples of the powder taken at frequent intervals while the grinding proceeds.

The preparation of a fine sample for analysis from the rough sample brought to the laboratory, is generally effected by a repetition of the above processes: a pestle and mortar, steel or bone spatula, and small metal sieves, made of perforated zinc of various degrees of fineness, being the chief utensils employed. In the case of fibrous substances a pair of scissors and knife may also be required. The degree of fineness to be aimed at in the powder finally obtained must depend very much on the quantity to be taken for analysis. If the analysis is to be made on a small weight of material, the substance should be reduced to the finest possible powder; if, on the other hand, a considerable quantity of substance will be taken, a coarser sample will answer the purpose with sufficient exactness.

Some substances are too damp to admit of being reduced to a fine powder. A considerable weight of the rough sample should in such cases be dried, the loss of weight ascertained, and a fine sample prepared from the dry matter. The safest plan of proceeding is to perfectly dry a weighed quantity of the rough sample, and thus ascertain the total water present, and then determine water again in the fine sample when completed; the relation of the fine sample to the original substance is then exactly known. Indeed, when perfect accuracy is desired, it is nearly always necessary that the amount of water in the rough and fine sample should be ascertained, as in the process of grinding and sampling water is generally lost, sometimes to a large extent, and the analysis consequently yields results above the truth, being made on a drier sample than the original bulk. This source of error is too frequently overlooked.

If soluble phosphate is to be determined in a damp superphosphate, the manure should not be dried, but beaten up into a perfectly smooth paste. Damp guano must also not be dried in the ordinary way if nitrogen is to be determined in the dry matter; if, however, a weighed quantity of the damp guano is first slightly acidified with solution of oxalic or hydrochloric acid, it may then be dried without any practical loss of ammonia. As the

weight of the guano has been increased by the acid added, the relation of the fine sample to the original must be ascertained by a comparison of their actual weights. The guano should not be completely dried, else the product will be hygroscopic, and bear no constant relation to the original.

Determination of Nitrogen.—Nitrogen occurs in manures either in organic combinations, or as ammonia, cyanides, or nitric acid. Nitrogen in the form of cyanides is useless or even poisonous to plants, and should therefore not be reckoned among the available nitrogen of a manure. The total nitrogen present in the first three forms is conveniently determined by combustion with soda lime; in this operation the whole of the nitrogen is converted into ammonia, which is absorbed by a known volume of standard acid, its quantity being ascertained from the extent to which the acid is neutralized. A portion of the nitrogen existing as nitrates is also converted into ammonia during combustion with soda lime. Combustion with soda lime is the best method to employ in the analysis of farm-yard manure, sea weed, guano, fish manures, dried blood, shoddy, bones, and superphosphates containing bones or ammonia; it may also be used for ascertaining the value of ammonium salts if cyanides are absent.

A piece of hard combustion tube is drawn out and closed at one end, and the nitrogen bulbs fitted to it with a good cork. The length of the combustion tube will be about 10 inches. The tube is then nearly two-thirds filled with dry, coarsely powdered soda lime. The quantity of soda lime required for mixing being thus ascertained, a small quantity is left in the end of the tube, and the rest poured into a mortar and intimately mixed with the weighed substance taken for analysis. The tube is then refilled with the mixture, the mortar rinsed with small quantities of fresh soda lime, and more soda lime added till the tube is filled to about $1\frac{3}{4}$ inch from the open end. A small plug of ignited asbestos is then pushed against the soda lime, the tube rapped on its side upon the table so as to insure a passage for the gas along its whole length, the nitrogen bulbs containing the acid are attached, and the whole is then ready for the furnace.

If the substance to be analyzed contains ready-formed ammonia, as in the case of guano or ammonium salts, it cannot be mixed with soda lime in an open mortar without loss of ammonia taking place. The substance is in this case weighed in a small corked tube; the combustion tube is then half filled with powdered soda lime; on the surface of this the substance is poured from the weighing tube, and soda lime is then added to within 3 inches of the end. The substance is now inclosed in soda lime; a stout wire with a slight cork-screw twist at one end is introduced, and by passing this quickly up and down the mixture of the substance with soda lime is effected. Fresh soda lime is then placed in the front of the tube, asbestos added as before, and the bulbs at once attached. By reweighing the corked tube the amount of substance taken is ascertained.

The standard acid employed is a dilute solution of pure sulphuric acid, containing about 50 grams. of oil of vitriol per litre; its strength is accurately ascertained by precipitation with chloride of barium. To fill the nitrogen bulbs 20 c.c. of the acid are accurately measured from a pipette into a beaker; the point of the bulbs is then dipped into the acid, which is drawn into the bulbs by suction. The point of the bulb is rinsed into the beaker, and at the end of the combustion the bulb is emptied and rinsed into the same beaker, so that no acid is lost.

The combustion tube with the bulbs attached is placed in a gas furnace, consisting of a long row of Bunsen burners (Griffin's furnace is commonly used). Heat is first applied at the front of the tube, near the asbestos, and the part containing soda lime alone is first brought to redness. Burner after burner is then gradually lit till the whole tube is at a moderate red heat, which is continued till no more gas passes through the acid in the bulbs. The combustion tube is then allowed to cool, the sealed end is broken off, and air drawn slowly through the apparatus by suction applied to the nitrogen bulbs. The bulbs are then emptied and rinsed into the beaker containing the remains of the measured acid; the acid liquid is then neutralized by a standard solution of caustic alkali, a little tincture of litmus being added as an indicator. The number of cubic centimètres of alkali being known which are required to neutralize 20 c.c. of the standard acid, we have only to subtract from this number the cubic centimètres required at the end of the combustion, to find by difference the extent to which the acid has been neutralized by ammonia. The value of a cubic centimètre of standard alkali in ammonia or nitrogen being known, it is easy to calculate the percentage of nitrogen in the substance.

The standard alkali is usually a very dilute solution of caustic soda, of which 100 c.c. neutralize 20 c.c. of the standard acid. In Germany baryta water is commonly used, and is said to give a sharper reaction than soda. When baryta water is used the burette has a tubulure at its lower end, the baryta water being introduced below the float. The upper end of the burette is connected with the air space of the baryta reservoir, so that, as the baryta water is run out, air free from carbonic acid enters.

As ammonia is decomposed at a high red heat, an excessive temperature must be avoided in a combustion. For the same reason the tube should not be too long, and there should be a sufficient amount of carbonaceous matter present to produce a continuous current of gas. In the case of such substances as shoddy, which require a prolonged heat, it is useful to mix a small quantity of pure starch or sugar with the substance (See Church's "Laboratory Guide").

Dr. Voelcker has for a long time employed iron tubes in his combustions; they are made of gas-pipe welded at the end. It must be ascertained in every case that the welded end is air tight before employing a new tube. As air cannot be drawn through the tube, a little oxalate of calcium should be placed

in the closed end before introducing the soda lime. When, at the close of the combustion, heat reaches the end o the tube, the oxalate evolves carbonic oxide gas, which sweeps out the other gases remaining in the tube.

It is frequently desirable to determine the amount of *ammonia* present in a manure. Supposing that cyanides and organic nitrogenous matter are absent, this is readily done by boiling the substance in a retort with water and caustic soda, collecting the ammoniacal distillate in a known volume of standard acid, and then calculating the amount of ammonia from the extent to which the acid is neutralized. If cyanides are present caustic soda must not be employed, as a part of the cyanogen is thus transformed into ammonia; in such cases milk of lime must be substituted for the soda. Distillation with milk of lime is the best method of determining ammonia in commercial ammonium salts in all cases where cyanides are present. If organic nitrogenous matter is present, as in a manure partly made from bone, it is safest to distil with freshly calcined magnesia.

When ammonium salts are tolerably pure, the quantity of ammonia present may be directly determined in the form of platinum salt (see article Ammonia); the ammonia in the distillates just described may also be determined in this form if the ammoniacal gas be collected in hydrochloric acid. Determination with chloride of platinum is, however, except in the case of pure ammonium salts, more tedious than the alkalimetric method just described.

In Germany considerable use is made of Knop and Wolf's method of decomposing ammoniacal compounds with a bromated, strongly alkaline solution of sodium hypochlorite. In this reaction the nitrogen of the ammonia is evolved in a free state; from the volume of nitrogen gas produced the amount of ammonia present is calculated. This mode of determination requires a special apparatus —Knop's azotometer. The method is speedy, and when used with proper precautions accurate. It must be borne in mind that urea, and a few other nitrogenous organic bodies, also give up a large part of their nitrogen when treated with an alkaline hypobromite or hypochlorite.

Gas liquor is the only fluid manure with which we are concerned; its value depends on the amount of ammonia it contains. The ammonia is usually chiefly present as carbonate, but a part always exists in non-volatile combinations, and in some cases, depending on the character of the coal, these non-volatile salts actually preponderate. Gas liquor is often valued on the basis of its specific gravity, but this is no certain guide to the ammonia present. According to Gerlach, the total ammonia present in gas liquor bears on an average the following relation to its gravity:—

Specific Gravity.	Ammonia. Lbs. per 100 Gallons.
1·007	6·58
1·013	13·16
1·020	19·74
1·027	26·32
1·034	32·90

The amount of volatile ammonium compounds (carbonate and sulphide) present in gas liquor is readily determined by simple distillation into standard acid after the plan already described. The total ammonia present is ascertained by distillation with slaked lime; soda must not be used, as cyanides are usually present.

The determination of *nitric acid* is only required in the analysis of nitrate of sodium, or of manures of which it forms an ingredient; as, however, the use of nitrate of sodium in mixed manures is largely increasing, the determination of nitric acid becomes of considerable importance.

The value of nitrate of sodium depends on the amount of pure nitrate present; as this is usually very large (about 95 per cent.), it is a common practice to determine the impurities present—the water, chlorides, sulphates, lime, and insoluble matter, and to find by subtraction the amount of pure nitrate. The total quantity of impurity per cent. is known as the "refraction."

The amount of nitric acid present in nitrate of sodium may be determined directly by several methods, some of which we will briefly describe. A simple and convenient plan is to thoroughly mix 5 to 6 grams. of dry, finely powdered quartz with 1 gram. of the powdered dry nitrate in a platinum crucible; place the whole in the water oven for half an hour, and then weigh. The covered crucible is next heated to very low redness for thirty minutes and again weighed. The difference between the two wei hings is the nitric acid originally present.

Another simple method which has been recommended, is to determine in the first place the chlorine in the nitrate of sodium by the volumetric silver method, and then to convert all nitrates into chlorides by ignition with chloride of ammonium. Chlorine is again determined after ignition, and the increase in its percentage, multiplied by 1·52, gives the nitric acid originally present.

The nitric acid in mixed manures may be determined by conversion into ammonia, and estimation in that form. The manure is in the first instance extracted with water; this solution will contain all the nitrates that may be present. The watery solution is made strongly alkaline with pure caustic soda or potash, and the nitric acid reduced to ammonia by the action of a mixture of zinc and iron; the ammonia is then distilled off, and collected in standard acid as already described. In Harcourt's process, 50 grams. of finely granulated zinc, 25 grams. of iron filings (purified by sifting, and ignition in a covered crucible), and 20 c.c. of potash solution, specific gravity 1·3, with 20 c.c. water, are employed for ·5 gram. of nitre, and the whole at once distilled. The metals unacted on may be used for the next operation. Some of the German chemists employ a coil of thin zinc and iron ribbon; this is placed in the cold, strongly alkaline solution for six to twelve hours, at the end of which time the conversion into ammonia is complete. The coil is then removed, and the ammonia determined with hypobromite of sodium, or by distillation.

A volumetric method is sometimes employed for the determination of nitric acid: it is very convenient when speedy results are required, but must be used with some caution. A solution of indigo is first prepared from the paste of sulphindigotate of sodium, sold in commerce as "indigo-carmine;" 14 grams. of the fresh paste may be dissolved in a litre of water, and the solution filtered. The strength of the indigo solution is next ascertained by experiment with a standard solution of nitre. The nitre solution is made by dissolving 1·011 gram. of pure dry nitrate of potassium in 1 litre of water. 10 c.c. of the nitre solution are placed in a wide-mouthed flask of about 150 c.c. capacity, and to this is added 25 c.c. of pure distilled oil of vitriol; the acid being added speedily, but without agitation, so as to form a layer at the bottom of the flask. When the acid has been introduced the flask is at once brought under the burette containing the indigo, and indigo solution run in rapidly with agitation of the flask, till the blue colour of the indigo is no longer destroyed. The quantity of indigo taken in the first experiment is considerably less than that which the nitre is capable of oxidising. In the next experiment 10 c.c. of nitrate solution are placed in the flask, and a rather larger quantity of indigo added than was used in the first experiment; a volume of oil of vitriol, equal to the united volumes of indigo and nitrate solutions, is then added as suddenly as possible, and the whole immediately mixed. If the colour one minute after mixing is cinnamon or golden, another experiment must be made with more indigo; if the colour is greenish or blue, less indigo must be taken in the next experiment. The tint desired for final reaction is a brownish shade, which on pouring the liquid into twice its volume of cold water becomes just perceptibly green. The tint yielded by dilution is far more distinct than that first seen. It is essential that in every experiment the oil of vitriol used should exactly equal the united volumes of the nitrate and indigo. When the relation of the indigo to the standard nitre solution has been ascertained by successive approximations, the former should be diluted so that 10 c.c. of indigo equal 10 c.c. of nitre. The strength of the indigo should be redetermined from time to time. To make it keep better the solution may be heated for some time to 70° C., or sulphuric acid in the proportion of 2 per cent. by volume added; both of these operations should precede standardizing.

To determine nitric acid in a manure by this method, a cold water extract of the manure is prepared, and brought to a known volume, a strength somewhat similar to that of the standard nitre solution being aimed at. 10 c.c. of the solution are then treated with indigo exactly as just described, till the maximum quantity of indigo oxidisable by the nitrate is ascertained. With weak extracts 20 c.c. of solution may be taken for experiment.

The reaction of the nitrate and indigo only takes place at a certain temperature (above 100°); when, however, the oil of vitriol is of full gravity (1·84), and the temperature of the laboratory not unpleasantly low, the heat produced during mixture will be quite sufficient. Should the colour of the indigo fade slowly during the reaction, it is a sign that artificial heat must be employed; the flask should then be placed in a chloride of calcium bath after adding the oil of vitriol; the temperature of the bath should be about 130°.

The oil of vitriol must be distilled acid, and contain neither nitrous nor sulphurous acid. The former is detected by adding 20 to 30 c.c. of the acid to its own volume of distilled water previously coloured by indigo; if the blue colour is discharged nitrous impurities are present. Nitric and nitrous acid may be removed from oil of vitriol by adding to it some crystals of oxalate of ammonium, and heating for an hour to near its boiling point. Sulphurous acid may be removed by heating the acid for several hours in an open flask to near its boiling point.

In the presence of certain organic substances, or of any easily oxidisable body, the results yielded by indigo become too low. For further particulars respecting the indigo method the reader is referred to the *Chemical News*, xxxv. 45, 57.

Determination of Phosphoric Acid.—The phosphoric acid in bone, coprolite, and in nearly all natural phosphates, exists in a state insoluble, or scarcely soluble, in water. In superphosphates, on the other hand, the phosphoric acid is chiefly in a form soluble in water. The analysis of these two classes of phosphates will require separate consideration.

The choice of a method suitable for the analysis of an insoluble phosphate depends chiefly on whether iron and aluminium are present, and if so in what quantity. In genuine Peruvian guano, in clean bone or bone ash, and in many of the apatites, iron and aluminium are absent, or present in very small quantity; such phosphates are conveniently analyzed either by the silver or uranium method. In the case of guano or bone, the portion taken for analysis must be first ignited at a low red heat till all organic matter is destroyed. As guano generally contains phosphate of ammonium, and in some cases quite a considerable quantity of this salt, it is necessary, when perfect accuracy is desired, to mix the guano before burning with twice its weight of a mixture of equal parts carbonate of sodium and nitrate of potassium; this insures the whole of the phosphoric acid in the ash being in the tribasic condition.

If the silver method is employed, the phosphate should be dissolved in nitric acid, an excess of acid being avoided. In the case of an apatite containing fluorine, the solution must be evaporated to dryness to expel the fluorine. The evaporation to dryness should also always be performed in cases where silica is present. It is important, however, that the residue should not be too strongly heated, else a portion of the phosphoric acid will lose its tribasic condition; a long-continued heat at the temperature of boiling water is the safest proceeding. The residue left by evaporation is redissolved in nitric acid and water, and the silica separated by filtration. The clear nitric solution is then treated with excess

of nitrate of silver. Oxide of silver is finally added, and digestion in the cold continued till the fluid is neutral. The whole of the phosphoric acid is now precipitated as phosphate of silver, the calcium remaining in solution. The precipitate is collected, washed, dissolved in a little nitric acid, the silver precipitated with hydrochloric acid, the chloride of silver removed by filtration, and the phosphoric acid precipitated by the addition of ammonia and magnesia mixture. The precipitate of ammonio-magnesic phosphate may be collected after six hours' standing, washed with ammonia water, dried, ignited at a high temperature, and the resulting pyrophosphate weighed: 100 parts of the ignited precipitate contain 63·964 parts of phosphoric acid. Magnesia mixture is best made with 55 parts of crystallized chloride of magnesium, 70 parts of chloride of ammonium, 650 parts of water, and 350 parts of liquid ammonia; 10 c.c. of this mixture are sufficient to precipitate 1 gram. of phosphoric acid.

The volumetric uranium method is largely used on account of its speed, and in cases where iron and aluminium are absent gives results of sufficient accuracy. About 35 grams. of nitrate of uranium are dissolved in 900 c.c. of water, a portion of the solution transferred to a burette, and its value in phosphoric acid accurately ascertained by several experiments with pure phosphate of calcium. For this purpose a nitric acid solution of phosphate of calcium, free from iron and aluminium, is prepared, using as little nitric acid as possible, and the amount of phosphoric acid present accurately determined by the silver method. A known portion of this solution, containing ·1 gram. phosphoric acid, is then taken, 10 c.c. of a solution of acetate of sodium (prepared by dissolving 100 grams. of acetate of sodium in 900 c.c. of water, and adding 100 c.c. strong acetic acid) are then added, which should produce no precipitate, and 10 to 15 c.c. of the uranium solution run in. A drop of the mixture is removed to a white porcelain plate, and a slight quantity of powdered ferrocyanide of potassium added; no reddish colour should be produced. The addition of the uranium solution is then continued in small quantities, testing as before after each addition. When the ferrocyanide produces a reddish brown tint, the whole of the liquid is to be heated to near boiling in a water bath, and a drop again tested with ferrocyanide. If the ferrocyanide then gives a just perceptible reaction the experiment is completed; if the reaction is, on the other hand, distinct, the next experiment must be made with rather less uranium. When the strength of the uranium solution has been ascertained by several accordant experiments, it is finally diluted, till 1 c.c. equals ·005 gram. phosphoric acid, and is then ready for use. It is well not to standardize the uranium solution till it has been made a few days, as a basic salt is apt to be deposited.

In employing the uranium method the solution of the phosphate in nitric acid is brought to any known volume (say 250 c.c.), and a measured portion containing about ·1 gram. of phosphoric acid taken for the analysis. The liquid is treated with 10 c.c. of acetate of sodium, and then with uranium solution, as above described. If the exact point of first reaction with ferrocyanide is not hit in the first experiment, a second portion of the fluid must be taken. The solution of the phosphate should contain as little free nitric acid as possible. If the addition of the acetate of sodium causes a small precipitate (phosphate of iron or aluminium), the liquid must be filtered, and the clear filtrate used for the uranium experiment. The precipitate should be washed, dried, burnt, and weighed; 47 per cent. of its weight may be reckoned as phosphoric acid. When, however, the precipitate produced by acetate of sodium becomes at all considerable, the method cannot be relied on for really accurate results.

In the analysis of coprolite, or of ferruginous phosphates containing little alumina, the oxalate-citric method may be adopted. The solution of the phosphate in hydrochloric acid, previously freed from silica by evaporation to dryness, is cautiously neutralized with dilute ammonia, with constant stirring, till a very slight permanent opalescence is produced. A drop or two of solution of oxalic acid is then added, which clears the solution, and then oxalate of ammonium, till it ceases to produce a precipitate. The whole is then brought nearly to boiling, filtered, and the precipitate washed with hot water. The precipitate may be dried, burnt, and weighed; it gives the amount of calcium (weighed as carbonate) contained in the mineral. The filtrate is then treated with citric acid, the quantity depending on the amount of iron present. Ammonia is finally added in excess, which, if sufficient citric acid has been employed, will produce a clear lemon-yellow solution. Magnesia mixture is now added in distinct excess, and the whole allowed to stand twenty-four hours. The precipitated ammonio-magnesic phosphate is collected, washed with ammonia water, ignited at a high temperature, and weighed. It is stated by some chemists that the precipitate of ammonio-magnesic phosphate obtained in this method is not always pure. Dixon recommends adding a rather considerable excess of magnesia mixture, and after long standing, to pour off the fluid, wash slightly, redissolve in a small quantity of hydrochloric acid, and reprecipitate with ammonia. Some chemists redissolve the washed precipitate in acetic acid, add acetate of sodium, and titrate with uranium solution. This latter modification is especially used in France, where the use of oxalate of ammonium is omitted, and the hydrochloric solution of the phosphate is at once treated with citric acid in such quantity that ammonia may be added in excess without occasioning a precipitate. Magnesia mixture is then added (prepared from chloride of magnesium), and the precipitated ammonio-magnesic phosphate is, after long standing, washed, redissolved, and titrated with uranium, as above described.

In cases where much alumina is present, the above-mentioned methods are apt to give low results, from the solubility of the ammonio-magnesic phosphate in aluminic solutions; in such cases recourse

must be had to the molybdic method. This method, when properly conducted, is of great accuracy, and is advantageously adopted in all analyses of impure phosphates. It is necessary that silica should be removed by evaporation to dryness, and also that no chlorine should be present. Ferruginous phosphates are best dissolved in strong hydrochloric acid, the solution evaporated to dryness, and the dry residue treated with dilute sulphuric acid, and again heated till all hydrochloric acid is expelled. This is known by the residue losing all its yellow colour, and by a further small addition of sulphuric acid giving no smell of hydrochloric acid when heat is applied; a great excess of sulphuric acid is to be avoided. The residue is then dissolved in nitric acid and hot water (if a considerable excess of sulphuric acid is present the nitric acid may be omitted), and filtered from the insoluble sulphate of calcium and silica; the filtrate should occupy only a small volume. The molybdic solution is prepared by dissolving 75 grams. of molybdate of ammonium in water and ammonia, so that the total volume is 500 c.c.; this is then slowly poured into 500 c.c. of strong nitric acid. The solution should stand some days before use. About 100 c.c. are sufficient to precipitate ·1 gram. of phosphoric acid. The solution of the phosphate is mixed with such a volume of the molybdic liquor as is judged sufficient, and stood in a warm place (50°) for an hour. A small portion of the clear liquid is then removed, and treated with its own volume of the molybdic solution; should this produce a precipitate, a further quantity of the precipitant is added to the main bulk. When an excess of the molybdic solution is present, the whole is allowed to stand for four hours in a warm place. The bright yellow precipitate is then collected, washed with warm water containing a quarter its volume of molybdic liquor, and finally dissolved off the filter with hot ammonia, using as little as is necessary. The ammoniacal solution is then treated with hydrochloric acid, till the precipitate formed redissolves but slowly on stirring. Magnesia mixture is then added, and finally ammonia. The precipitate of ammonio-magnesic phosphate is collected after twelve hours' standing, washed with ammonia water, dried, and ignited at a very high temperature in the gas blow-pipe. Owing to the bulk of the molybdic solution, it is not convenient to take much more than ·2 gram. of phosphoric acid for a determination. If the solution operated on contains much free sulphuric acid, it will be found necessary to add some nitrate of ammonium, to insure complete precipitation by the molybdic liquor.

In the analysis of superphosphate it is required to ascertain the amount of phosphoric acid that is soluble in water, and the amount that is insoluble. Superphosphates contain monocalcic phosphate, and often some free phosphoric acid; both of these are soluble in water. The aqueous solution may also contain the phosphates of aluminium and iron, dissolved in the free phosphoric or sulphuric acid present. Such a solution is partly decomposed on dilution, and still more on boiling, the phosphates of aluminium and iron being precipitated. On cooling, the precipitate slowly redissolves to a greater or less extent. These facts teach us that superphosphates should be extracted with cold water, and that the extraction should be made with repeated small quantities of water, if the maximum amount of soluble phosphate is under all circumstances to be obtained. It is usual with some chemists, after extraction with cold water, to boil the undissolved residue, and add the solution thus obtained to the previous cold extract; by this plan the amount of soluble phosphate found is further increased. The justice of this mode of proceeding is very questionable, as the soluble phosphate obtained by exhaustion with boiling water did not exist as soluble phosphate in the manure, but has been produced by the splitting up of insoluble phosphates at a boiling heat into more acid and more basic compounds.

In the case of superphosphates made from natural phosphates nearly free from aluminium and iron, it is sufficient to place 10 grams. of the manure in a mortar, add a little distilled water, and rub lightly with the pestle, so as to break all lumps without grinding. Transfer the whole to a litre flask, and add water to the mark in the neck, then shake for a few minutes, and filter. The determination of soluble phosphate is made on 100 c.c. of the filtrate.

If the manure, however, contains much alumina and ferric oxide, the weighed quantity is rubbed with a very small quantity of water, transferred to a filter, and washed by repeated additions of water, each washing being allowed to run through before another is applied. When the washings cease to be acid, the filtrate is cleared with a few drops of nitric acid, and diluted to any volume that is desired.

The solution of the superphosphate may be analyzed by the oxalate-citric method already described, except in cases where a considerable amount of alumina is present; when such is the case the molybdic method is the only one yielding perfectly exact results. The presence of much alumina may be known by boiling the cold aqueous extract of the superphosphate; if the solution is sufficiently dilute the phosphate of aluminium is thrown down at a boiling heat. In pursuing the oxalate-citric method the solution of the superphosphate may be at once treated with oxalate of ammonium, the addition of ammonia being unnecessary; the remainder of the process has been already described.

The most usual way of determining phosphoric acid in the solution of a superphosphate is by the volumetric uranium method: 100 c.c. of the solution (corresponding to 1 gram. of the manure) are treated with 10 c.c. of the acetate of sodium solution, and the rest of the process conducted as already described. If the acetate of sodium produces a precipitate of phosphate of aluminium and iron, it is well to take 400 c.c. of the solution, add 40 c.c. of the acetate, filter, and take 110 c.c. of the filtrate for the titration with uranium. The phosphate of iron and aluminium is to be washed, dried, burnt, and weighed, and the phosphoric acid calculated therefrom added to that found by uranium. If the

precipitate by acetate of sodium is small, the method will be satisfactory; but if it is large, the results cannot be strictly relied on.

Manufacturers who are continually making manure in similar proportions, and from *perfectly similar materials*, may analyze the products so obtained by the uranium method without regarding the iron and aluminium present. For this purpose the amount of phosphoric acid present in the aqueous solution of a superphosphate is in one or more cases accurately determined, and at the same time the amount of uranium required for its precipitation; the value of the uranium solution in phosphoric acid is thus ascertained for the particular class of manure in question. By this means speedy determinations of approximate accuracy may be obtained.

The free phosphoric acid present in a superphosphate may, according to J. Kolb, be determined by ascertaining, first, the total amount of phosphoric acid soluble in water; and, secondly, the amount of phosphoric acid found in solution when the same weight of the superphosphate is extracted with 80 per cent. alcohol. As free phosphoric acid is soluble in alcohol, and monocalcic phosphate is split up by alcohol into phosphoric acid and dicalcic phosphate, we are enabled to arrive at the quantity of free phosphoric acid and monocalcic phosphate originally present by the following calculation:—

Let x = free phosphoric acid.
y = phosphoric acid existing as monocalcic phosphate.
P = total phosphoric acid extracted by cold water.
Q = total phosphoric acid extracted by alcohol.
Then $P = x + y$. $Q = x + \frac{1}{2}y$.
And $x = 2Q - P$. * $y = 2(P - Q)$.

The *insoluble phosphate* of a superphosphate consists partly of unacted-on mineral phosphate, and partly (in the case of manures made from ferruginous or aluminous materials) of phosphate of iron and aluminium formed in the manure out of soluble phosphate by a subsequent reaction already described. This phosphate of iron and aluminium is known as "reduced phosphate." It is undoubtedly of greater agricultural value than unacted-on mineral phosphate, and many attempts have been made to determine satisfactorily the amount of reduced phosphate in a manure. All such attempts have, however, failed to yield trustworthy results; a description of the methods proposed may therefore be omitted.

The insoluble phosphate in a superphosphate is best ascertained by making a determination of the total phosphoric acid in the manure, and then subtracting from this the amount of soluble phosphate. If the superphosphate is tolerably free from aluminium, the total phosphoric acid may be ascertained by digestion with hydrochloric acid, and treating the solution by the oxalate-citric method. When much alumina is present, the molybdic method, or Flight's barium method, must be resorted to if strict accuracy is desired. The cases, however, in which this will be necessary are very rare; insoluble phosphate having only a small value a somewhat rough determination of its quantity is generally sufficient.

* This equation is incorrectly given in Kolb's paper as $x = 2(Q - P)$.

In reporting the results of an analysis of superphosphate, the whole of the soluble phosphoric acid may be reckoned as monocalcic phosphate, if no determination of free phosphoric acid has been made. It is usual, however, in England to express the soluble phosphoric acid as equal to so much tricalcic phosphate rendered soluble; and a manure is said to contain so much "soluble phosphate"—that is, $Ca_3P_2O_8$ rendered soluble. This is a very convenient form of expression. The term "biphosphate" (CaP_2O_6) should be avoided, as such a substance has no existence in the manure, and the term is not recognized by scientific chemists. The whole of the insoluble phosphoric acid in a superphosphate is calculated as tricalcic phosphate, and reported as "insoluble phosphate."

Determination of Potash.—This base is always weighed in the form of the double chloride of potassium and platinum. The quantity of material taken for analysis should contain ·2 to ·3 gram. of potash. The process employed depends upon the nature of the substances associated with the potassium salt. If the salt is pure chloride of potassium, or contains in addition only chloride of sodium, the conversion of the potassium into the form of platinum salt may be at once effected. For this purpose the watery solution of the salt is mixed with solution of tetrachloride of platinum, and evaporated nearly to dryness in a small basin over a water bath. The chloride of platinum must be added in excess of that required to convert all the sodium and potassium present into platinum salts; the necessary excess of platinum may be reckoned to be present when the moist residue left on evaporation yields a dark orange solution when treated with a few drops of water. The moist crystalline mass left in the basin by evaporation is to be treated with alcohol of 80 to 90 per cent., and removed to a very small filter of Swedish paper, which has been previously dried in the water oven and weighed. The precipitate is then washed with alcohol (90 per cent.) till the washings have for some time come through colourless. The filter and its contents are then dried in the water oven and weighed: 100 of the precipitate contain 19·27 of potash. The larger is the amount of sodium present, the greater should be the excess of chloride of platinum used. When much chloride of sodium is present, the salt in the basin should also be wetted with water before treatment with alcohol.

If the potassium or sodium is present as sulphate, it is usual to remove the sulphuric acid by treatment with chloride of barium or strontium, before proceeding to the determination with platinum. If chloride of barium is used the excess of barium has afterwards to be removed; this is most conveniently done by adding pure crystallized oxalic acid to the liquor. If only a very small excess of barium has been employed, a quantity of oxalic acid three and a half times that of the substance taken will be sufficient. The whole is evaporated to dryness in a platinum basin, and the residue gently ignited. On treatment with water, and filtering, the alkalies

are obtained in solution as carbonates, the barium being left undissolved; hydrochloric acid is then added to the filtrate, and the determination with platinum proceeded with.

A simpler plan is the use of chloride of strontium; in this case the excess of strontium need not be removed, as strontium forms a soluble salt with chloride of platinum. The concentrated solution of the potassium salt is precipitated with a small excess of chloride of strontium; the liquid is treated with about half its volume of alcohol and filtered; the precipitate is washed with weak spirit; the filtrate and washings concentrated, and treated with chloride of platinum.

Messrs. WALLACE, TATLOCK, and CLARK state that the removal of sulphuric acid before the determination with platinum is unnecessary, and that the error occasioned by its presence may be effectually met by adding pure chloride of sodium, which prevents the formation of any free sulphuric acid.

When potassium salts are associated with calcium and magnesium, it is usual to separate the other bases before proceeding to determine the potash. The separation is effected in the same process which removes sulphuric acid, namely, successive treatment with chloride of barium and oxalic acid. Messrs. WALLACE, TATLOCK, and CLARK do not remove magnesium or calcium, but treat the potassium salt at once with excess of chloride of platinum. The moist residue of platinum salts finally obtained is then treated, not with alcohol, but with a few cubic centimètres of strong chloride of platinum solution; after standing an hour with occasional stirring, the precipitate is collected, and washed twice with a few drops of platinum chloride, and finally with alcohol. This simple method is said to give good results.

When potash has to be determined in a complex manure, the aqueous solution is best precipitated with excess of chloride of barium; carbonate of ammonium and ammonia are then added, which precipitate with the barium (if it has been used in sufficient excess) all the phosphoric acid which may be present. The filtrate is evaporated to dryness in a platinum basin, ignited to expel ammonium salts, and then treated with oxalic acid exactly as already described.

MERCURY, *Quicksilver.—Mercure, vif-argent*, French; *Merkur, Quecksilber, Anteril*, German; *Hydrargyrum*, Latin. Atomic weight, 200. Symbol, Hg.

The most marked characteristic of mercury, and that in which it differs from all other metals, is its fluidity at ordinary temperatures. It is this property, coupled with its silvery whiteness and metallic lustre, which probably determined its popular name, "quicksilver." PLINY styles the native metal *Argentum vivum*, the metal reduced from an ore, *Hydrargyrum*.

This metal and some of its uses appear to have been known at a very early period of the world's history. ARISTOTLE relates that DÆDALUS gave motion to a wooden Venus by means of a current of mercury. DIOSCORIDES describes a method for its reduction from cinnabar (at that time termed *minium*), a process which is remarkable as being the first example of distillation. The metal was employed in gilding, much in the same way as at present, and the cinnabar was used as a pigment.

The Greeks drew their supplies of mercury from Spain, the mines of which were known and worked seven hundred years before the Christian era.

PLINY seems undecided as to the true nature of the metal, since he thought that there was some radical difference between the mercury which was found in the virgin state and that obtained by the manufacture of the time. This doubt lurked in the minds of philosophers till towards the close of the seventeenth century, when both kinds were submitted to numerous distillations. BOERHAAVE distilled the same portion of mercury successively 500 times, and the products were found to coincide in weight and all the then known properties. Still, at this period, on account of its fluidity, it was regarded as an imperfect or semi-metal, containing a principle regarded as pure vitrifiable earth—the silica of modern times. The fact of this terrestrial principle conferring solidity upon such bodies as contain it in abundance, being directly opposed to the fluid condition of mercury, induced BECCHER, an investigator of the first half of the seventeenth century, to infer the existence of another principle, a *mercurial earth*, which was supposed to possess weight and volatility to a very great degree. He then regarded quicksilver as a compound of three substances—namely, the vitrifiable, the inflammable or phlogistonic, and the mercurial. On the introduction of experimental research and deduction, the nature of bodies came to be regarded in a simpler but truer light, which overthrew the hypothetical obscurity that pervaded all chemistry up till that time.

The observation that mercury could be solidified by cold was made by the academicians of St. Petersburg during the intensely cold winter of 1759, and was the first step towards removing the notion of its semi-metallic nature; and inquiries to which the announcement of the fact gave rise in the hands of PALLAS, HUTCHINS, BIEKER, BLAGDEN, and several others, led the way to its recognition as a true metal, and elementary body.

PREPARATION.—Several methods are known for the production of mercury from its combinations, many of which are practised on the large scale, and will consequently be described when treating of its smelting; but as these do not yield a pure metal, reference will be here made only to the methods that are calculated to afford such a product.

The mercury of commerce, which usually is contaminated with variable portions of lead, tin, and bismuth, may be distilled with one-tenth of its weight of cinnabar; and provided the distillation be carefully effected, the foreign impurities will be found in the retort, in the form of sulphides, after the pure mercury has passed over into the receiver.

A purer product is, however, obtained when carefully prepared cinnabar or corrosive sublimate (mercuric chloride, $HgCl_2$) that has been cautiously sublimed, is distilled with one part of iron filings in a glass or earthen retort. It is best to cover the

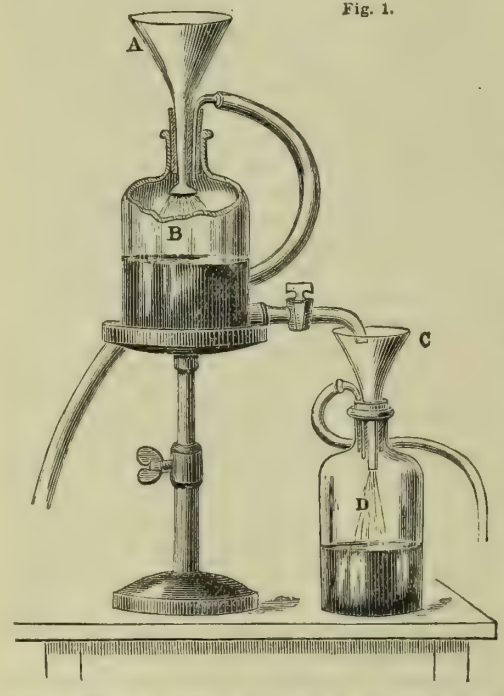
mercury with a thick layer of iron filings, to prevent the foreign metals being carried over with the vapour, or by spirting.

Sometimes agitation with concentrated nitric or sulphuric acids has the effect of rendering mercury much purer.

BIANCHI recommends boiling the impure mercury with $\frac{1}{87}$th of its weight of mercurous nitrate dissolved in water, or with a small quantity of dilute nitric acid; or the agitation of the metal for some days with strong oil of vitriol, till the acid no longer becomes turbid or takes up any body in solution.

The most ordinary impurities are lead, zinc, and tin, and common dirt and dust. A. LEEDS has arranged a very convenient apparatus (Fig. 1) for removing these with little trouble to the operator. It consists of a glass funnel, A, capable of holding

Fig. 1.



5 or 10 lbs. of mercury, the tube of which is cut off at a point just below the india-rubber stopper of the bottle, B. Cotton wool is jammed into the tube until it fills up the neck, and bulges out at the bottom of the funnel. A short glass tube, bent at right angles, passes likewise through the india-rubber stopper, and is connected with a water air-pump. The bottle is two-thirds filled with dilute nitric acid (1 part of acid and 4 or 5 parts of water). The impure mercury poured into the funnel, A, is drawn through the cotton plug in a multitude of streams, leaving its mechanical impurities behind it, and passes as a fine rain through the acid below. The foreign metals, if not in too large quantities, are removed by solution in the acid, and the pure mercury collects below. It is then run off through a stop-cock into the second funnel, C; and after being thoroughly dried by suction through another plug of cotton wool, is caught and preserved in the bottle, D. A very short time suffices for the almost automatic purification of a large quantity of mercury.

To ascertain purity of the metal it is only necessary to dissolve a portion in an excess of nitric acid, evaporate the solution, and heat the dry salt to redness; or fuse the metal with pure sulphur, and sublime the product in a glass flask. In either case nothing should remain if the metal be pure; but if a residue appear, the impurities are proportionate to its weight. Observation has led to the adoption of a simpler, but less reliable test than the above; it is this—that pure mercury when dropped upon a smooth, but slightly-inclined surface, breaks up into drops which retain the spherical form; but if contaminated with tin, lead, or such adulterants or impurities, the form of the globules will appear elongated, so as to present or leave *a tail*.

ULEX purifies mercury by agitating 2 lbs. with half an ounce of a solution of ferric chloride, having the specific gravity 1·48. After ten minutes' shaking, the mercury is washed with water, dried, and the finely-divided globules reunited by the application of a gentle heat.

Properties.—Mercury is fluid at all temperatures between —39°·4 C. and its boiling point, which is variously estimated by different experimenters as ranging between 346° C. (CRICHTON) and 360° C. (DULONG and PETIT)—DALTON estimating it at 349° C., and HEINRICH at 356° C. REGNAULT gives it as 357°·25 at a pressure of 760 m.m. Its vapour is colourless.

At —39°·44 (HUTCHINS) mercury solidifies, and while in this state permits of being beaten out under the hammer, welded, &c., like other metals. When the refrigeration is effected by means of solid carbonic acid and ether in a dish, and if the yet unsolidified portion be poured off, the metal adhering to the walls of the vessel will present well-defined octahedral crystals. Its density varies with the degree of temperature more than any other metal, owing to the freedom with which it expands. SCHULZE found it in the solid state to be 14·391; REGNAULT, 14·4. At 4° C. KOPP estimated its gravity at 13·594. BALFOUR STEWART, comparing water at 4° C. with mercury at 4° C., found this determination correct. At 26° C. KUPFFER found the specific gravity to be 13·535; CAVENDISH and BRISSON, 13·568; FAHRENHEIT, 13·757. KARSTEN determined its density at the ordinary temperature to be 13·559. Various researches show that this metal evaporates at common temperatures, as well in contact with air as *in vacuo*. This was proved by FARADAY by suspending gold leaf in a flask containing some of the metal, when, after a few weeks, the lower portion of the leaf will appear amalgamated. KARSTEN found that at 0° C. mercury gives off enough vapour to develop the image on a daguerreotype plate held over it at a convenient distance. This observation was corroborated by REGNAULT, who succeeded in producing a daguerreotype picture by the vapour evolved by mercury at —13° C. BRAME affirms that sulphur in a finely-divided condition, as when pre-

cipitated from a state of vapour, is much more delicate than gold leaf. By its aid he found that at 12° C. the tension of the vapour rises to the height of 3 feet, and even higher than this; though, in the latter case, the delicacy of the then known tests was inadequate for its detection—but that, in fact, its atmosphere has no limits. This investigator also found that in air and vapour of sulphur, the vapour of mercury diffuses itself according to the law which governs other gases.

Merget has corroborated and extended these observations by using as a test, paper coated with ammoniacal silver nitrate, and has thus succeeded in proving the vaporization of the metal at temperatures as low as —44° C., the volatilization being uninterrupted even by congelation.

The specific gravity of mercury vapour referred to air as unity is 6·976, Dumas; 6·7, Bineau. The theoretical density is 6·933. Taking hydrogen as unity, the theoretical specific gravity is 100.

The property which mercury possesses of expanding with remarkable regularity through a long range of temperature renders it peculiarly adapted for estimating the sensible heat of bodies. Hence its use in the thermometer was proposed by Halley in 1697. Mercurial thermometers were, nevertheless, not constructed till after 1726.

The experiments of Regnault give the mean coefficient of cubical expansion of mercury between 0° and 100° C. as 0·00018153. Matthiessen gives it as 0·0001812.

Between —38° and 0° C. the gradation is less regular, although the difference is so slight that it may generally be disregarded; but at temperatures above the boiling point of water the coefficient of expansion increases somewhat rapidly. Thus while the true coefficient at 100° C. is 0·00018305, at 140° C. it is 0·000186, and at 200° C. 0·000189.

The power of mercury for conducting heat is in the liquid state 53·5 (Calvert and Johnson), silver being 1000. Its specific heat, solid, ·03113; liquid, 0·03192.

Mercury is not acted upon when exposed to air, oxygen, nitrogen, nitrous or nitric oxide, or carbonic acid gases. If shaken with water, ether, oil of turpentine, or fatty unctuous matters, it loses its metallic appearance, and is converted into a grey *æthiops per se*, in which the metal is not altered but *deadened*—that is, reduced to minute and isolated globules by the interposed stratum of the compounded matter. Ordinary mercurial ointments retain the metal in this state, but so finely divided as to render its detection by the unaided sight impossible. In a well prepared ointment the mercury forms uniform globules, having a diameter of about $\frac{1}{1000}$th of a line. In course of time the mercury in this finely divided state becomes oxidised.

When pure, mercury is tasteless and inodorous, although a peculiar odour has been observed from it when rubbed between the fingers. Poured upon dry bodies, it does not wet them like other liquids, but flows off in drops, except in the case of the metals with which it forms amalgams. On this account it is designated sometimes in old writings, *aqua non madefacions manus*—water that does not wet the hands. Kept at a temperature approaching ebullition in contact with air, it suffers oxidation slowly. Water is not decomposed by it. The nitrous, nitric, iodic, chloric acids, &c., easily oxidise it without the aid of heat; sulphuric acid, when diluted, has no action upon the metal, even when aided by heat; but concentrated acid, at a high temperature, readily converts it into a mercurous sulphate, sulphurous acid being given off. With selenium, sulphur, phosphorus, chlorine, bromine, and iodine, it unites with facility. It quickly combines with the noble metals—also with tin, lead, bismuth, zinc, and most of the soft metals, giving rise to amalgams which often possess particular interest. This is the case, more especially in a manufacturing sense, with the amalgams it constitutes with gold, silver, platinum, as they are available in the smelting or abstraction of these metals from the gangue in which they may be distributed. Indeed, a chief portion of the mercury annually extracted is devoted to this special application, so that a distinct relation between the yearly production of gold and mercury may be traced. Besides this application it has many others, such as gilding, plating, and the like. Many of its compounds are valuable in medicine, painting, &c.

Ores of Mercury.—The minerals into the composition of which mercury enters are by no means numerous. The metal itself occurs native in the form of fluid globules scattered through its gangue. The quicksilver mines of Almaden in Spain, of Idria in Carniola, of Wölfstein and Morsfield in the Palatinate of Rosena in Hungary, Sala in Sweden, and New Almaden in California, supply the virgin metal. In some places native mercury is so plentifully dispersed through the ores, that when an opening is made it escapes, and trickling out, collects in considerable quantities at the bottoms of the levels.

A native amalgam of silver, amorphous and crystallized, is also met with. Not unfrequently this mineral occurs in the form of flattened plates. *Arquirite*, an argentiferous amalgam of great value, is found in considerable quantity in the province of Coquimbo in Chili. It contains 13·5 parts of mercury, and as much as 86·5 per cent. of silver. Indeed, this is one of the chief ores of silver in the rich mines of Arguiros. An amalgam of gold, analyzed by Schneider, and which occurred along with platinum ore from Columbia, contained mercury 57·40, gold 38·39, and silver 5·0. Native amalgams of lead, containing selenium, have been analyzed by Rosé.

Horn quicksilver—mercurous chloride, Hg_2Cl_2, or native calomel—is found associated with the other ores of quicksilver at Idria, at Deux-Ponts, in Spain, and elsewhere. It is a yellowish or ash-grey mineral, sectile, and subtranslucent. Sometimes it occurs as a crust, or forms granular concretions. At other times it crystallizes in four-sided prisms. Its specific gravity is 6·482, whilst that of the powdered calomel of the shops is 7·14, and that of the crystallized factitious subchloride is 7·2.

Iodides, bromides, and selenides of mercury also occur, but rarely. The iodide has been met with in Mexico, associated with the selenide.

The principal ore of mercury is mercuric sulphide, HgS—the *zinnober* of the Germans and *minium* of Pliny. The colour of native cinnabar varies from cochineal red to brownish-red and leaden grey. The streak is scarlet, and the lustre usually adamantine. The density of this mineral is 8·098, and when pure it contains 86·29 parts of mercury with 13·71 of sulphur. Specimens of the purest ore have occasionally all the richness of hue which the best vermilion presents.

The following table shows the percentage composition of the cinnabar from various quarters of the world:—

	Mercury.	Sulphur.	Bituminous matters.	Gangue.	Water.	Carbon.	Silica.	Alumina.	Iron.	Copper.	Lime.	Magnesia.	Total.	
Japan,	84·50	14·75	—	—	—	—	—	—	—	—	—	—	99·25	Klaproth.
"	79·30	14·50	—	—	—	—		5·67		—	0·63	—	100 10	Dalzell.
Idria,	51·80	8·20	6·80	32·0	3·20	—	—	—	—	—	—	—	102·00	Lebererz.
Idrian Swaore,	81·80	13·75	—	—	0·73	2·30	0·65	0 55	0·20	—	—	—	99·00	Klaproth.
Neumarktel,	85·00	14 25	—	—	—	—	—	—	—	—	—	—	99·25	"
Wolfstein,	18·00	—	—	—	—	—	—	—	73·31	—	—	—	91·31	Bealey.
Almaden,	37·84	16·22	—	—	—	—		35·12	—	—	—	—	89·18	"
"	37·75	16 22	—	—	—	—		35·12	—	—	—	—	—	"
"	36·94	15 97	—	—	2·58	—		42·79	—	traces.	—	—	98·28	Dalzell.
"	41·79	16·72	—	—	—	—		41·49	—	—	—	—	100·00	"
California,	69·36	11·38	—	—	—	—	14·30	0·61	1·23	—	1·40	0·49	98·77	Bealey.
"	70·13	11·21	—	—	—	—	14·52	0·61	1·23	—	1·40	0·49	99·59	"
"	70·23	11·21	—	—	—	—	14 52	0 61	1·23	—	1·40	0·49	99 59	"
"	72·00	12·80	—	—	1·20	—	—	—	14·0	—	—	—	100·00	Dalzell.

Geologically, the ores of mercury occur amongst stratified deposits. The volatility of the metal may account for its not being met with in any large quantity in crystalline or igneous rocks. Thus, it is found most abundantly in the independent coal formation, and in beds lying between primitive argillaceous schistus and chlorite slate, associated with quartz, calcareous spar, spathic iron, and copper pyrites. In the famous quicksilver mines of Almaden in the province of La Mancha, a few miles from the frontier of Estremadura, which have been worked for many centuries, the veins traverse micaceous transition schists and sandstone grit, intersected here and there by granitic and porphyritic eruptions. A portion of the Almaden ore is extremely rich; but the larger proportion is so intermixed with quartzose and argillaceous gangues, that the yield is not over 10 per cent. of metal. At Quença in New Granada, Durasno in Mexico, and in some of the Peruvian mines, the mercurial ore occurs in the red sandstone above the coal; whilst at Deux-Ponts, at San Juan de la Chica in Peru, and in some other localities, it is placed in the subordinate porphyry. The mines of Idria are worked in a friable compound of dark carbonate of lime and argillaceous schist. These mines were discovered by accident in 1497.

The subterranean passages of these mines are extensive; but owing to the loose and friable nature of the ground large excavations are impossible. Their greatest perpendicular depth, taken from the entrance of the shaft, is about 800 feet; but as the galleries advance horizontally under a high mountain, the depth would be much greater if measured from the surface of the hill. The mine was formerly entered either by descending the shaft in a bucket, or by zig-zag ladders. Now, however, the entrance is through a large iron gate, by a horizontal passage to a descending flight of 757 steps, cut in the limestone rock, and provided with a hand-rail. At the bottom of these steps there is a small chapel, in which the miners perform their devotions, and from which a labyrinth of passages opens out. In some of the galleries the heat is so intense as to be almost insupportable. The noxious inhalations of the metal speedily become so offensive that the visitor is glad to make his escape. The ascent is performed by a perpendicular shaft.

Some of the ore yields 50 to 60 per cent. of metal. The richest qualities are termed *stahlerz;* and the poorer, bituminous sulphide, averaging only 10 per cent., are called *zeigelerz.* Besides the quicksilver works there is a manufactory of cinnabar.

The mercury mines of the Palatinate are not equal in richness and importance to those of Idria and Almaden. The workings at Drey-Kœnigszug, at Potzberg near Kussel, give an annual yield of about 30 tons. The ore is sandstone intimately mixed with mercuric sulphide, and the depth to which the explorations have been carried exceeds 660 feet. There are several still smaller mines in Hungary, Bohemia, and other parts of Germany. The quicksilver mines of Huancavelica in Peru, the products of which are employed in the treatment of the gold and silver ores which abound in that neighbourhood, have been worked since 1570. Up to 1800 their produce was 53,700 tons of quicksilver.

The Californian mine of New Almaden is situated a few miles from the coast, about midway from San Francisco and Monterey, and in one of the ridges of Sierra Azul mountain. The mouth of the mine is a few yards down from the summit of the highest hill that has yet been found to contain quicksilver, and is about 1200 feet above the neighbouring plain, and not much more above the ocean. This hill extends longitudinally in a north-west direction, decreasing in height; and in various parts of it, for several miles, traces of the ore have been found,

and some openings have been made which promise to be valuable. This range of hills consists of a variety of rocks; the prevailing one is a greenish talcose rock, which seems to embrace the bed of ore at the New Almaden mine both above and below. The ore is interspersed through a yellow ochreous matrix, which forms a bed 42 feet in thickness, dipping north-westerly at an angle of about 45°. The richest ore is at present found in the upper part of the bed; the poorest ores being taken from the lowest portion.

This mine, known to the aborigines from time immemorial as *a cave of red earth* from which they obtained paint for their bodies, was first discovered to contain quicksilver during experiments made by some Mexicans to smelt the ore for the purpose of obtaining *gold*, which they supposed it to contain. The Californian metal comes into the market in wrought-iron bottles, screw stoppered, and holding 75 lbs. each. The bottle itself weighs about 25 lbs.

The present entrance to the workings is by a horizontal shaft and railway 1200 feet long. The large masses of rich and compact ore, some of which weigh as much as 20 lbs., are separated from the small fragments, which are mixed up with yellowish earth and clay. The latter are pounded, kneaded up with water, and dried in the sun; thus baked they are called *adóbés*. The smelting furnaces, with their condensing chambers, are situated a mile and a quarter from the entrance to the mine. Each range consists of a fire chamber 3 feet by 5, placed at the end of a series of eight or ten chambers, 7 feet long, 4 wide, and 5 high. The range is built of brick plastered inside, and protected against expansion by heat by iron rods passing from wall to wall, and secured with screws and nuts. The tops are of boiler plate, luted with salt and ashes. The first or fire chamber is separated from the second or ore chamber by a network partition of fire-brick. The third chamber communicates with the ore chamber by a square opening at the right upper corner, and this first condensing chamber with the second by a similar opening at the left lower corner, and so on; the top openings being on the right, and the lower openings on the left, alternately. From the last condensing chambers the vapours pass into a wooden hose, in which there is a continuous shower of cold water, while any uncondensed matters pass into the open air through tall wooden flues. The floors of the condensers are guttered, and by these the mercury flows into an open conduit, from the end of which it pours over a brush into the iron bottles already described.

The lumps of cinnabar and the adóbés are piled like bricks in the second chamber; a wood fire is lighted in the furnace, and the flame plays through the brick network on the ore. Each ore chamber when fully charged contains 10,000 lbs. of cinnabar, to exhaust which requires sixty hours. At the present time lime does not appear to be used in the reduction of the ore. Ruschenberger conceives that the addition of this substance would increase the yield, but not, he adds, sufficiently to pay the cost of the earth.

Assay of Mercurial Ores.—The methods generally followed are distillation of the product, whether it be oxide, chloride, sulphide, selenide, or iodide, with caustic lime.

From 15 to 25 parts of lime may be taken, according to the richness of the ore. This is intimately blended in a mortar with the finely ground ore, together with a tenth of the weight of fine charcoal, and the whole introduced into an earthen or hard glass retort, with a long neck surrounded with cloths, on which a stream of water may be kept flowing for the purpose of condensing the vapour. The beak of the retort should likewise be inserted in a flask kept cool by wet cloths. The distillation may be carried on over a gas flame, or by means of a small charcoal fire and sand bath. All the mercury is transported into the neck of the retort in the state of vapour, where it condenses, and trickles into the receiver. When the materials have been carried to dull redness, the fire is removed, and any globules which may remain in the neck of the retort made to flow over into the receiver by tapping it gently, or introducing a small brush; and after the whole has been collected the product is weighed. In this way the yield of mercury is ascertained with a degree of accuracy which will be dependent upon the carefulness of the operator.

Eshka prefers to mix the finely pulverized ore with iron filings, and to volatilize the mercury in a porcelain crucible covered with a concave, close-fitting gold lid, the hollow of which is filled with cold water. The crucible is heated for ten minutes in the point of a flame. The gold lid is then removed, the water poured off, the convex side washed with alcohol, the lid dried, and then weighed. The increase of weight in the gold represents the amount of mercury in the sample. If the mercury is abundant it may form absolute globules on the surface of the gold; care must then be taken that no loss occurs in washing.

Reduction of Mercurial Ores on the large scale.—There is, with a few exceptions, very little diversity in the manner in which the smelting of mercurial ores is carried on. It is strange, however, that in the case of the largest and most important *lode* in the world, that of Almaden, the comparatively rude and inefficient method of working invented by Juan Alonsa Bustamente more than two hundred years ago, should still be followed in all its details.

Figs. 2 and 3 represent a section and plan of the kind of apparatus employed, which is known as the *butyrone* or *aludel* furnace. It consists of a circular or polygonal chamber, A, about 4 feet in diameter, and divided into two compartments by a perforated brick arch about 9 feet from the top. The heat is obtained from brushwood introduced at the aperture, C, into the fireplace, *a*, and the smoke is carried off in part by the chimney, D. A door, E, in the side of the cylinder, and an aperture, F, at the top, are used to introduce the charge of ore, the volatile products of which escape into the condensing media by a system of openings, G, and

which communicate with files of condensers of earthenware, called *aludels*, H, connected one with another, as represented in Fig. 4. These are laid on two planes of brick work, inclining to one another, supported on arches represented in Fig. 2. Where the two planes meet is a channel or gutter, I,

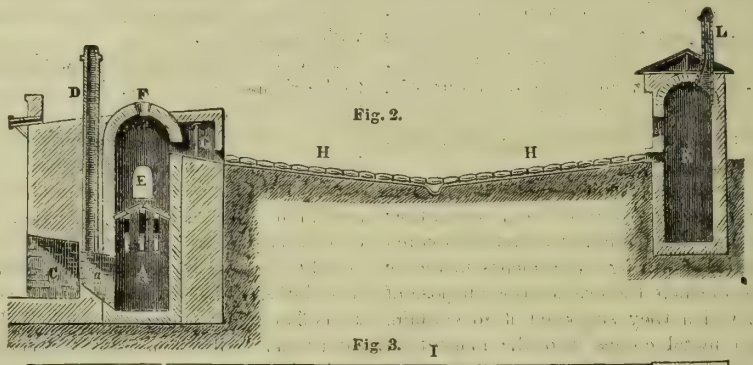
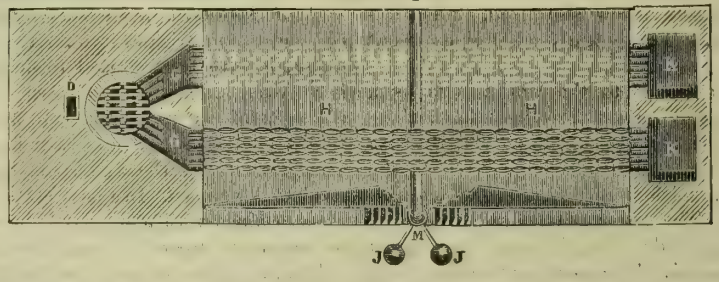


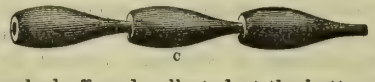
Fig. 2.

Fig. 3.



leading to a conduit, M, in the brickwork, and thence by wooden pipes at the bottom to the receiving basins, J J, partly filled with water, and fixed in the floor of the smelting room. During the passage of the distilled vapours through the several files of aludels, the metal which condenses flows for the most part into the aludel which crosses the channel, I, and issues into the latter by a hole in its under part; the uncondensed products pass into the upper part of a condensing chamber, K, and are conducted towards the bottom by a screen, where a cistern of cold water receives the metal. Such portions as diffuse themselves in the chambers are deposited on the walls in form of soot, and are from time to

Fig. 4.



time brushed off and collected at the bottom. Sulphurous and other gases pass off by the chimney, L, but sometimes a second chamber is above the arch of the first, in which a further quantity of the metal is retained. Whatever is collected in this way is filtered, in order to purify it from other matters, and the dross is worked up with loam and fine or powdered ore into bricks, and subsequently distilled over again. The charge of ore for this furnace averages from 220 to 270 cwts., and is divided into three varieties, each of which occupies particular places in the furnace. The larger pieces of the sandstone rock, slightly impregnated with cinnabar, and called *soleras*, are placed on the arch immediately above the fire. Being too poor to be worked by themselves, and requiring too much labour for preliminary dressing, they are worked off in this part of the furnace. Above the *soleras*, about 22 cwts. of rich mineral are laid on, then some poor ore in small fragments, and the remaining space is filled with the dross from the aludels and condensing chambers, and some fine ore previously worked up with some clay and moulded into bricks. The door in the side, and also the aperture in the top, are then secured by the doors, and covers, and luting. After this the adapters are arranged in proper order on the inclined planes, and the joinings secured by clay luting. The number of these vessels being so large, a good deal of time and labour is required for this work. There are 6 files in each bench, and 44 vessels in each file, making for the entire furnace about 528. From the aperture of the furnace to the condensing chamber the length is about 65 feet, so that each aludel is more than 18 inches long. All things being ready, the fire is lighted and kept in active ignition by the supply of fresh brushwood. An abundant flame is thus produced which passes up through the apertures in the arch of the furnace, and heats, first the *soleras*, and subsequently the remaining contents, and drives the whole of the metal into the aludels, volatilizing it with the sulphur in the form of sulphurous acid with a little sulphuric acid. According as the aludels become heated by the vapours, they begin to act more effectually the part of a series of chimneys, and so draw off the products more freely. The fire continues successively for twelve days to work off the charge, after which time it is permitted to die out; and three days further are allowed to cool the earthen

adapters before they are detached, and the portion of mercury in them collected. This work also consumes a good deal of labour, as each receiver, after being detached, has to be brought to the channel midway to be emptied. Any metal shed in the carriage runs along the incline, but is not lost; it becomes soiled, however, so that it is necessary to submit the whole to a purifying process. That adopted is very simple: the metal is poured on the floor of the room destined for the work, which being slightly inclined towards one end, the mercury flows down clean and bright into a receiver, and leaves the dross and soot behind it adhering to the floor. A good deal of metal remains in the residue; hence it is carefully collected and worked up in the next charge. Each charge affords from 2500 to 3000 lbs. of mercury; sometimes, when the ore is a richer kind, as much as 6000 lbs. are obtained; but the manager tries to average the ore so that the yield may be about the first-mentioned quantity. If the charge be enriched by using more of the purer ore, the loss in mercury is considerably greater than if only an average kind be worked; besides, the trouble arising from the cracking of the lutes securing the connection of the aludels, and their renovation, is multiplied. Besides the mercury, another substance is found to encrust the earthen cones, which Proust found to contain—

	Per Cent.
Finely-divided mercury,	66·0
Mercurous chloride,	18·0
Cinnabar,	1·0
Ammonium sulphate,	3·5
Calcium sulphate,	1·0
Free sulphuric acid	2·5
Carbon, or soot,	5·0
Water,	2·5
Loss,	0·5

Proust estimates the extent of its formation at about 40 lbs. per charge, or in its content of metal equal to 1·500 of the weight of the rich mineral wrought, and attributes the presence of the chloride to its being contained in the ore, and volatilized as such. This loss is, in part, avoided by mixing some quicklime with the *schlich* and clay in making the bricks which occupy the upper space near the dome of the furnace. Cast-iron cylinders, bent, and surrounded with water, have been tried at Almaden as a substitute for the aludels, but their use was abandoned in consequence of their being rapidly corroded by the free acid, although the mercury was found to condense very well in them.

A portion of the Almaden mines, probably that now called Little Almaden, was worked by the Romans. Pliny speaks of *Sisapo, a territory of Bœtica, the mine of minium there forming a part of the revenues of the Roman people.* The modern town is built over the principal mine, the entrance to which is close to the houses, and the ascent and descent of the miners effected by ladders. The produce of the workings is drawn to the surface by mules, up a wide and well-constructed stone shaft.

The produce of the Almaden mines is packed in cylindrical cast-iron bottles, which are closed with a screw stopper. Each bottle contains 3 Spanish arobas, making 70 English lbs. nett per bottle. But the weight charged by the importers is on an average only 69 to 70 lbs., arising from the tret of 4 lbs. per every 104 lbs.; and 1 lb. draft being allowed, and the tare being fixed at 8 lbs., whilst the real tare averages 16 to 17 lbs.

Method of Reduction at Idria.—This famous mine was discovered so far back as 1497, but the working of the ore was very irregularly prosecuted for nearly a century afterwards; and even then there was no fixed establishment, but the ore and utensils necessary were carried about in the forests to where the charcoal burner had chosen the site for his *meiler*, in order to make the heat of the burning wood available for the reduction of the ore. A number of earthen pots, with narrow necks, were filled with the ore, mixed sometimes with lime; the mouth was then stopped with a clay plug, so as to retain the charge, but allow the fluid metal to flow out into a wide-mouthed vessel, into which the charged one was inverted. As many of these as would fit in the base of the charcoal heap were arranged as described, and the clay or soil raised about the subjacent condensing pots, the connection between the two luted, and the wood arranged in the usual way for charring. During the combustion of the wood the heat was sufficient to set free the metal which collected in the bottom pot. This method of distillation *per descensum* was extremely wasteful. In 1635 a fixed establishment was erected, and the gallery furnace analogous to that at the Palatinate adopted; in 1750 the Almaden system was introduced; and, finally, at the close of the last century, for the aludel furnace the present arrangement was substituted.

The commencement of the present Idrian process is the assortment of the ores into two classes, according to the size of the pieces. All from the size of a cubic foot to that of a nut belong to No. 1; smaller pieces, and the dust, to No. 2. In No. 1 are further subclassified—the poorest portions, yielding only about 1 per cent.; the pure sulphide, yielding nearly 80 per cent.; and fragments of various richness, averaging from 1 to 40 per cent. The subclasses of No. 2 consist of—fragments from the mine, yielding from 10 to 12 per cent.; particles separated on the sieve, yielding about 32 per cent.; and lastly, the *schlich* obtained from the washings, containing 8 parts of the metal in 100.

There are at present three kinds of furnace in use—the Almaden furnace, the distilling apparatus about to be next described, and the "flamofen" (reverberatory furnace).

Figs. 5 and 6 are a plan and elevated section of the great distillatory furnace erected at Idria. In the latter figure only one of the furnaces is seen, although there are two in the same block, with a double row of condensing chambers, as represented in the plan. Fig. 7 is a section of the roaster. *a a* are the fire doors: *b*, the hearth where the fuel is consumed, and above which is the body, *d*, of the furnace, divided by perforated arches into three compartments, the top one being in communication with the first condensing chamber on either side by

flues, *c*. There are six chambers at each side of the furnace, F, G, H, I, K, L, the connection of one with another being placed alternately near the top and bottom, with the view of bringing the vapour over as much space as possible. Each of these chambers has a curved bottom leading to the outlet, S, by

Fig. 5.

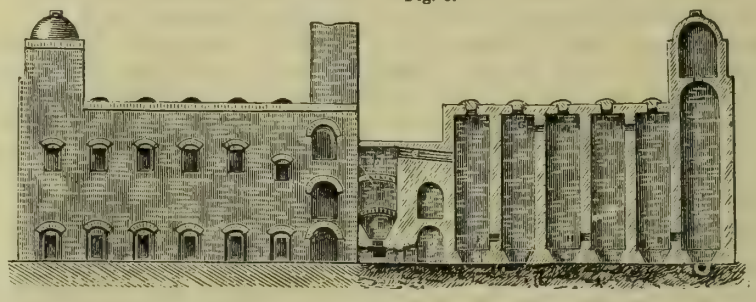
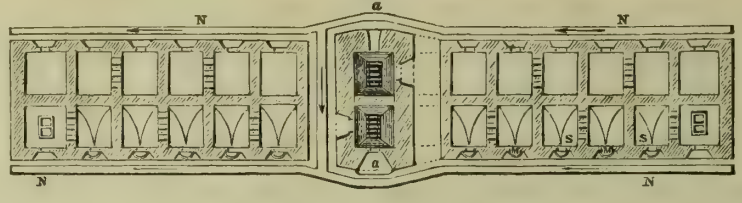
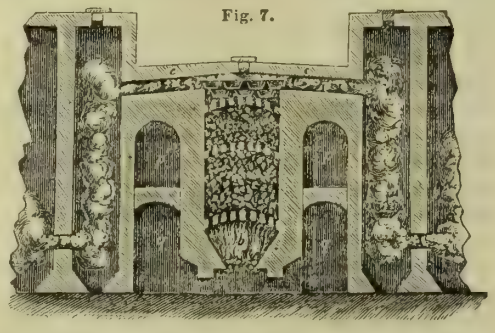


Fig. 6.



which the condensed metal flows out into a receiver, M M, when it is conducted by a conduit, N N, into the main tank. They have likewise an aperature at the top, which is closed, as also that at the base, during the period that the furnace is working. The last chamber in the series is usually furnished with a number of flanges, or inclined boards, which reach in a slanting direction almost to the opposite wall, upon which a stream of water is continually falling from the top, so that the vapour, as it ascends through it, follows a sinuous course, and deposits

Fig. 7.



the last trace of metal as it meets the flanges. *p*, *q* are arches which conduct air to the fire and interior of the furnace, for the oxidation or burning of the sulphur. By side doors, opening into the several compartments of the furnace, the ore is introduced; these are closed whilst the charge is being fired. The largest and poorest pieces of ore are placed on the first arch, and the smaller ones in overlying beds till this part is full: in the next the smaller fragments, and the upper compartment receives a number of earthen trays filled with the fine powder or *schlich*. All the spaces being thus filled, and the doors and other apertures secured and luted, a brisk fire of beech or fir wood is made on the hearth, *b*, and maintained till the furnace acquires gradually a cherry-red heat; it is kept at this degree for ten to twelve hours, during which the distillation lasts. The high temperature of the developed vapours, coupled with the great height of the furnace (about 30 feet) and the number of chambers that are in connection with it, create from the first a quick draught, which is sustained while the distillation continues. The furnace is allowed five or six days to cool and condense the metal, at the end of which time the upper apertures are opened, the portion condensed on the bottom drawn off, the walls brushed down, the separated mercury collected with the rest, and the grey powder and cinnabar gathered and put to one side, to be worked up in the next charge. This done, preparation is made to recharge and repeat the same process just described. One charge a week is the most that can be worked. A gang of forty men are employed in the charging, and the work lasts three hours.

The yield of each charge averages 80 to 90 quintals of metal (a quintal is 108 lbs.).

Lastly, the mercury is filtered through ticking cloth, and is then packed in cast-iron bottles for exportation. Each bottle contains 60 lbs. The furnace is 180 feet long and 30 feet high.

The "flamofen" present the advantage of being continuous in their operation (thus saving the loss of five to six days while cooling is going on), and of permitting the use of very poor ore. They besides entail less labour and consume less fuel.

The hearth of the furnace, E E (Figs 8 and 9) slopes from back to front; above it, at B, is a hopper for feeding in the ore, whilst below, at A A, is an opening through which the burnt ore can be raked out.

At the end of the furnace is the first condensing chamber, D; from hence the vapours pass by two cast-iron tubes, J J (which are parallel and slightly inclined), into the chambers, L, M, and finally into N. Here they meet a third tube, J, exactly like the lower ones, and inclined parallel with them, an

Fig. 8.

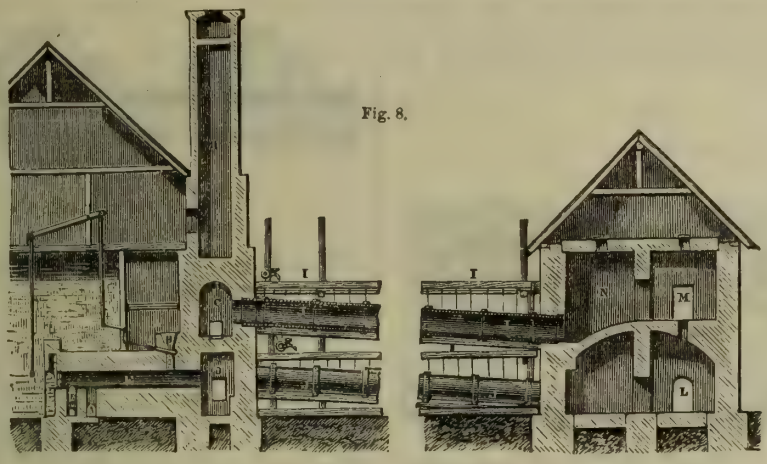
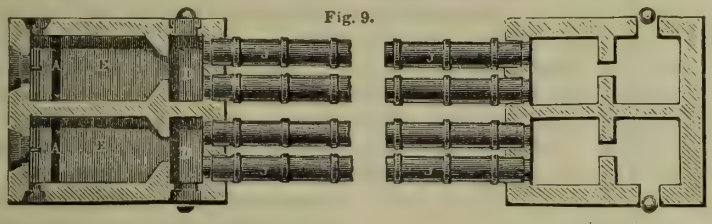


Fig. 9.

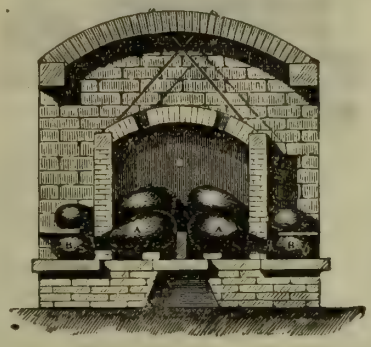


arrangement which insures that all the mercury deposited within it shall flow back into the chamber, N. The third condensing tube opens into the chamber, C, at the base of the chimney shaft, H. The condensation of the mercury is hastened by streams of water which trickle on the outside of the condensers from the troughs, I I.

In the Almaden and Idria works the principle of the changes is the removal of the sulphur by its combustion into sulphurous and sulphuric acids; and with this view the furnaces are constructed so that the air is freely drawn through them at the temperature necessary to cause the expulsion of the sulphur. In the duchy of Deux-Ponts the same ends are attained—not, however, by roasting, but by the addition of bodies which take the sulphur from the valuable metal, by a process of chemical decomposition. Lime is the substance always used, it being the most plentiful and cheapest; but scales or grains of iron would likewise answer.

In the duchy of Deux-Ponts mercurial ores, mixed with lime, are heated in earthenware retorts furnished with receivers of the same material. A vertical section of the furnace gallery of the Palatinate is shown at Fig. 10. A A represent earthen cucurbits with their receivers, B B. Each of the former is filled about two-thirds with a charge containing ore and quicklime in the proportion of 60 to 16, and the receivers are at the same time half filled with water. The retorts are arranged in a double row, one above the other. In this way from 30 to 52 cucurbits are included in one *gallery*. The fire, which is from pit-coal, is placed on a grate beneath them, and a draft is secured by means of apertures in the arched roof. When the mercurial gangue is sufficiently calcareous, it is only necessary to moisten and distil it. As soon as the mass in the retorts is exhausted, the contents of the receivers are emptied into a wooden basin standing over a bucket; the object of this

Fig. 10.

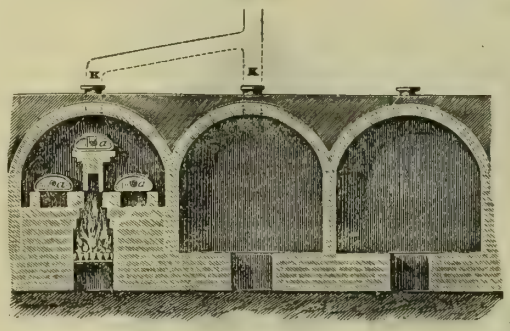


operation being to draw off, along with the water which falls over the sides of the bowl, all the black sulphide with which the metal is mixed up. This black matter is afterwards taken up, dried, and again distilled with excess of lime.

Method pursued at Lansberg.—One other metallurgic apparatus for the reduction of mercurial ores remains to be described. It is in use at Lansberg,

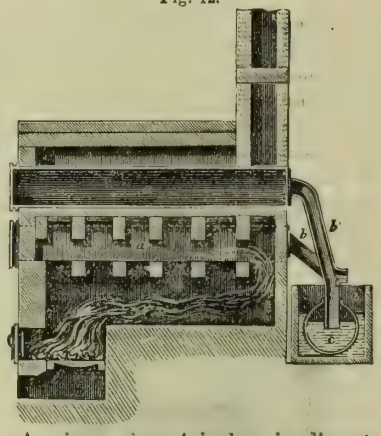
near Obermoschel, in the Bavarian Rhein-Kreis. It was designed by URE. Fig. 11 is a section parallel to the front elevation of three arched benches of retorts. Each bench contains three of these vessels, *a a a*, constructed of cast iron, and somewhat like those employed in the manufacture of coal gas; the

Fig. 11.



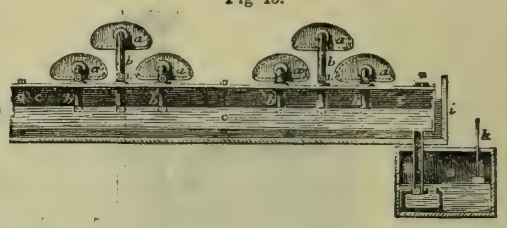
whole are set in masonry, the bottom of the uppermost retort being protected from the direct impingement of the flame by fire tiles. The dotted lines leading to K K show the direction of the chimneys. In Fig. 12 is represented in section the body of one of these retorts. The mouth on the right of the figure is closed with an iron lid, which is bolted, barred, and luted, after the charge has been intro-

Fig. 12.



duced. An iron pipe, 4 inches in diameter, and having a nozzle hole at L, dips into the main condenser, C, and the same arrangement is shown at another section at Fig. 13, where C C is the main condenser, which consists of a pipe 20 feet long and 18 inches in diameter. The backs of the retorts are shown at *a a*, and the eduction-tubes in the same figure at *b b*, dipping a short way beneath the surface of the water. At *z* is placed a water valve to obviate the risk of sudden expansion or condensation from inequalities of temperature, and at *i* is a water trough, or outer vessel of wood, in which the condenser is placed. The inclination of the condenser is towards the left, so as to favour the exit of the mercury by the vertical delivery tube, D, into the lock-up reservoir, *e*. The end of this tube dips from the first into a small cistern of mercury, and at *k* is shown a floating and graduated gauge

Fig 13.



rod, by which the quantity of mercury in the chest, *e*, may be always ascertained without the trouble of opening it.

Before charging the retorts, the ore is reduced to a coarse powder, then mixed with quicklime, and shovelled in: 6 or 7 cwts. of the mixture, a sufficient charge for each retort, can, with a proper amount of heat, be worked off in about three hours. The process is continuous.

Purification.—Mercury is commonly purified by distillation. This may be effected in a bent iron tube; or in an iron retort provided with a bent iron tube and connected with a receiver; or in strong glass retorts. If a glass vessel is used, the retort should rest in a deep sand bath, as much inclination as possible being given to its neck, which should be lengthened with a cylinder of stout paper. The end of the paper tube should dip into a receiver nearly full of water, which is also surrounded by water in a larger vessel. As soon as the mercury has distilled over and is cold, the water is poured off, and any trace of iron, or of oxide of mercury, which generally appears as a thin film, is readily removed by hydrochloric acid. The mercury is then well washed in water, dried at a gentle heat, or run through bibulous paper till it ceases to damp it; after which it may be passed through a cone of writing paper, having a very small aperture, which removes all traces of mechanical impurity. Or, instead of glass, a wrought-iron mercurial bottle may be employed. This bottle should never be more than half full, and must be fitted with an iron delivery tube, to the end of which a canvas pipe is attached, on which a jet of water is directed; the condensed mercury falls into a vessel. A second method is by treatment with strong sulphuric acid. This is best effected by covering the metal with its own volume of concentrated oil of vitriol in a flat glass or porcelain dish, stirring repeatedly with a glass rod, and leaving the metal and the acid in contact for six or seven days. Pure mercury, as has been already said, is not attacked by this acid, and digestion in the cold has merely to be repeated with successive portions of oil of vitriol as long as sulphurous gas is given off, or the liquid shows any symptoms of turbidity. It is certain that by this process even lead may be removed, although, under ordinary circumstances, that metal is but little attacked by strong cold sulphuric acid. But, in the first place, the lead in this case is in the form of amalgam, which

implies minute subdivision of its particles, and at the same time the tendency of the acid towards the lead appears to be increased *by the presence of the mercury*. Such metals as gold, silver, and platinum, which are not acted on by sulphuric acid, cannot of course be separated from mercury except by distillation.

MILLON has remarked that the presence of lead, tin, &c., hinders the process of distillation; while, on the contrary, the presence of platinum accelerates it. BARRESWILL has shown that this effect is due, in the first case, to a pellicle of oxide from the oxidisable metal, which, covering the surface of the mercury, prevents its volatilization. A layer of oil or resin acts in the same way.

Mercury in a tube or narrow glass vessel has a convex surface, owing to the mutual attraction of glass and mercury being at best but feeble; if, however, the metal be amalgamated with as slight a quantity as $\frac{1}{1000}$th part of lead, the convexity of the pure metal is destroyed, and the surface becomes even.

It has long been a matter of doubt and discussion whether this metal exercises any physiological effects upon the human system, analogous to those of its saline compounds. It is generally admitted that, when taken in compact masses, the metal does not exert a poisonous action, although it may occasion injury mechanically; but when in a finely attenuated state, or in vapour, it possesses the power of manifesting all the symptoms of a mercurial poison.

All the effects of mercurial poisoning are very frequently observed among the miners and smelters of this metal, as also in those who work with water-gilders, looking-glass and barometer makers. For the most part they appear as a kind of palsy, which first manifests itself by an unsteadiness in the arms, and which goes on till the movement becomes convulsive, and vertigo, loss of memory, and other cerebral disorders, which generally terminate fatally, follow.

Mercury is capable of combining with most of the non-metallic elements, and many of the compounds thus formed are capable of entering into further combinations; it has, therefore, a wide range of affinity, but in a manufacturing sense few of these compounds are important, although in a strictly scientific point of view, and also on account of their medicinal qualities, they sometimes attract a great deal of attention.

Mercury forms compounds which are bivalent, namely, the *mercuric* compounds, such as HgO, $HgSO_4$, HgI_2, &c.; and univalent compounds, namely, the *mercurous*, such as Hg_2O, Hg_2Cl_2, Hg_2I_2, &c. The mercurous compounds are readily converted into the mercuric by oxidising agents.

The principal compounds of mercury to be considered here are the sulphide—*cinnabar, vermilion*—the chlorides, oxides, iodides, *fulminating mercury*, and the ammonio-mercurial chlorides, known as fusible and infusible *white precipitate*. The oxides, though not the most important, will be noticed first.

OXIDES OF MERCURY.—There are two oxides of mercury, *monoxide*, or mercuric oxide, HgO, commonly known as red oxide of mercury, or red precipitate; and *suboxide*, mercurous oxide, Hg_2O, the grey oxide of mercury.

Mercurous oxide was first scientifically described in 1797; but was known probably long before that period as the *æthiops per se* of the pharmaceutists. There are several methods for preparing it; the simplest and readiest being the precipitation of a dilute solution of a mercurous nitrate by potassium hydrate; or it may be formed by disseminating calomel in water, and adding a proportionate quantity of a caustic alkali to the liquor, when mercurous oxide falls.

All the operations connected with this compound should be performed out of diffused daylight; and care must also be taken that the precipitation be complete, otherwise the substance thrown down will consist of a mixture of mercurous oxide, mercuric oxide, and metallic mercury.

After being thoroughly washed, to remove alkalinity, and dried in the dark, suboxide of mercury is a black powder having a disagreeable odour—GMELIN says it is devoid of taste and smell; it is insoluble in water and alkalies, soluble in nitric and acetic acids, and has a specific gravity of 10·6, HERAPATH; 8·95, KARSTEN. It is very rapidly decomposed when exposed to the light of the sun, into mercuric oxide and metallic mercury; but the same change, though slowly, is effected in the darkness. Heat resolves it into oxygen and metal. It is also decomposed by many compounds, the mercury being taken into other states of combination, and sometimes set free. The suboxide of mercury is converted to no particular use in the arts.

Mercuric Oxide, HgO.—This is the *precipitatum per se*, or calx of mercury, mentioned in old writings; it is analogous to the *hydrargyri oxidum rubrum* of modern pharmacy. Monoxide of mercury has an interest attached to it much greater than its application in the arts would merit, owing to the knowledge of its nature and composition being contemporary with the discovery of oxygen, the subversion of the old phlogiston theory, and the introduction and pursuit of a new and more enlightened system of chemical science. It was formerly prepared by submitting mercury to a high temperature (about 315° C.) in a narrow-necked flat-bottomed matrass, known as BOYLE'S *hell*, when, after about three weeks, the metal was slowly converted into oxide. This process is now, however, quite abandoned; oxidation of the metal, and subsequent precipitation of the oxide, being considered more effectual: 1 part of mercury is treated with 3 parts of nitric acid, specific gravity 1·20, in a flask on the sand bath, till perfect solution takes place, and the solution evaporated to dryness; the residue mixed up with another part of the metal, and the whole heated again as long as nitrous fumes are observed to pass off. The residue, which now appears a dull grey mass, is removed from the heat, mixed with a tenth of its weight of pure crystallized sodium carbonate, and the whole boiled with water for a quarter of an hour, when impure monoxide of

mercury settles to the bottom, and this by filtration and washing may be converted into pure mercuric oxide—*red oxide of mercury*. The mercuric nitrate alone may be submitted to heat in this operation, but a loss of nitric acid would take place; besides, the degree of heat is critical, so that it is more productive and less troublesome to proceed as above stated.

Oxide of mercury prepared by the action of heat upon a mercuric salt, forms a shining brick-red crystalline scaly powder, which, on being pulverized, acquires an orange tint. By the action of a moderate heat it changes to a vermilion colour, which passes as the temperature rises to a darker hue, approaching to black, but as the substance cools the natural shade is regained. The specific gravity of the red powder has been variously estimated, the number arrived at by PLAYFAIR and JOULE being 11·136. It is but slightly soluble in water, only one part being taken up by 7000 parts of this liquid; the solution, however, has a disagreeable metallic taste, and exhibits an alkaline reaction to delicate colour tests; but alcohol fails to dissolve it. When strongly heated (about 400° C.) it is resolved into its elements. Oxide of mercury obtained by precipitation is an amorphous yellow powder, and in this differs from that obtained by heat. There are also many other reactions wherein they behave differently.

Mercuric oxide is readily decomposed by several substances: even light is capable of resolving it into mercury and oxygen gas; heat and all organic substances produce the same effect, but much more quickly. On this account it is frequently employed in analysis to remove the last traces of carbon from a substance, and to oxidise sulphur into sulphuric acid. Phosphorus, sulphur, sulphurous acid, the alkali metals, stannous chloride, and several other bodies, decompose it, many of them with evolution of light and heat. The monoxide of mercury may be distinguished from the suboxide, first by its colour, and secondly by its solutions not giving a white flocculent precipitate with hydrochloric acid; it also produces with solutions of hydriodic acid, or of alkaline iodides, a beautiful scarlet precipitate of mercuric iodide, and which is characteristic compared with the dull green colour of the subiodide, or mercurous iodide, Hg_2I_2. Potash gives a yellow, and ammonia a white precipitate, both of which are sufficiently distinct from the black deposit that they afford in solutions of the suboxide of this metal.

It is stated that red oxide of mercury is occasionally adulterated with minium or red lead, sesquioxide of iron, and powdered brick. Such substances are readily detected by heating the substance to a dull heat; the mercuric oxide sublimes, and leaves the non-volatile matters behind.

SULPHIDES OF MERCURY. — *Mercurous sulphide*. Hg_2S, the *æthiops mineral* of the older chemists, was prepared by agitating a little water, sulphur, and mercury, in equal proportions, in a mortar, or at a slightly increased heat, till a black powder resulted. It can also be obtained by transmitting a stream of sulphuretted hydrogen gas through a dilute solution of mercurous nitrate in the cold, when a subsulphide of a black colour falls. Too high a temperature must be avoided, since it would resolve the mercurous sulphide into mercuric sulphide and metal.

Prepared by either method, this compound appears as a black, tasteless, inodorous powder, which is insoluble in water, in hydrochloric and dilute nitric acids. By heat it is resolved into mercury, and the red sulphide of the metal, cinnabar, HgS.

This compound is not prepared in any quantity, nor has it any application, excepting among veterinary surgeons, and even these are abandoning it for more appropriate agents.

Mercuric Sulphide, HgS—*Cinnabar, Vermilion.*—This is a much more important compound, though, like the former, medicinally inert. The character and composition of the native ore have been already explained. Only a small quantity of that mineral, however, is of sufficiently fine quality to permit of its being employed as a pigment. Chemically, there is no difficulty in forming it; but its value in the arts depends upon the richness of its colour, the exact conditions to insure which are as yet far from being understood. The following are some of the processes for its preparation:—

When sulphuretted hydrogen gas is passed to saturation through a solution of mercuric oxide, the white compound which appears at an early stage of the operation is destroyed, and the black precipitate then consists solely of mercuric sulphide, which, when collected, dried, and heated in a retort, yields a fine crystalline sublimate of cinnabar. These two bodies therefore, the black and the red, are allotropic modifications of one substance, HgS.

The process of LIEBIG consists in forming *white precipitate*, mercurammonium chloride, $HgNH_2Cl$, and digesting it with polysulphide of ammonium, obtained by saturating the common alkaline sulphide with sulphur. The colour of the product is afterwards improved by boiling with caustic potash.

KIRCHOFF recommends triturating 100 parts of mercury in a porcelain dish, with 23 parts of flowers of sulphur, chemical action being assisted from time to time by moistening the mixture with solution of caustic potash. A potash lie, containing 53 parts of solid hydrate in 53 of water, is next prepared, and in it the sulphurised mercury is warmed, and further triturated. The water must be replaced as it evaporates, and the operation continued for two hours. After this, and still with trituration, the red mass is evaporated to a thin paste, removing the heat at the moment when the red colour has attained its finest shade; for a few seconds, either too soon or too late, deteriorates the quality of the product. Too little heat fails to bring up the red to its utmost degree of brightness; and a little too high, or even too long continuance of the proper temperature, changes the colour to brown, and it can never be restored. The product, when cool, is *first* washed with a solution of potash, and *afterwards* with water.

It appears by the following table that the quantity of vermilion which can be obtained depends on the relative proportion of the substances employed:—

Mercury.	Sulphur.	Potash.	Vermilion.
300	114	75	330
"	115	75	331
"	120	120	321
"	150	152 yield	382
"	120	180	245
"	100	180	244
"	60	180	142

BRUNNER directs the trituration of 100 parts of mercury with 38 of sulphur. The æthiops so produced is next heated to 113° Fahr. with 25 parts of potash in 133 to 150 parts of water, and more liquid supplied as it becomes reduced by evaporation, the mixture being kept occasionally stirred. After a few hours the black substance begins to take a brown tint; and if the heat be maintained at 113° to 118° Fahr., this goes on brightening till it becomes a lively red. Whenever the mixture becomes gelatinous, more water must be added; for it is absolutely necessary for the success of the process that it be kept in as pulverulent a state as possible, and also that the heat rise not above 120° to 122° Fahr. When the product has attained the fine red required, and which happens in the course of eight hours, the fire is removed, and the contents of the vessel are left to cool slowly. The cinnabar is then removed, washed with water, and further purified by levigation from any mercury or black sulphide which might still remain. BRUNNER states that 100 parts of mercury, 40 parts of sulphur, and 40 of potash, afford 107 parts of vermilion little inferior to the finest native substance, and much superior to any obtained by sublimation.

Dutch Method of Making Vermilion. — It is well known that the monopoly of preparing this pigment was long held by the Dutch, who alone at one time possessed in Europe the secret of giving to it a rich scarlet colour. The process consisted of two parts: first, the production of a mixture of cinnabar, black sulphide, uncombined metal, and sulphur; and, second, the conversion of this into the pure vermilion.

The first part of the operation was to effect the combination in a flat polished iron pot, 2½ feet in diameter, and 1 deep. Into this 1080 lbs. of mercury and 150 lbs. of sulphur—equivalent to 87·8 of mercury and 12·2 of sulphur per cent.—were introduced, and the mixture stirred with an iron spatula very cautiously; because if the components were too briskly mingled, the combination would be too violent, and some of the substances would be lost. The black product of this operation, being reduced to powder, was next placed in hand jars capable of holding 1½ lb. of water—thirty to forty of them being constantly kept full. The subliming pots, three in number, which were made of pure sand and clay, and well luted outside, were each covered with a smooth iron lid, and placed in a furnace secured with hoops of iron, the position of the pots being such that the flame could play over two-thirds of their height. In the evening the operation of heating the pots was begun; and as soon as they attained a red heat the iron covers were removed, and a pipkinful of black sulphide thrown into each, and there left to crackle and burn. This emptying of the smaller pots into the larger was continued—sometimes two or more being emptied into the subliming pot at once—till, in the course of thirty-four hours, 410 lbs. had been emptied into each of the three. As each fresh portion of black matter was thrown in, the mixture took fire, and the flame rose from 3 to 6 feet above the edge of the pot. During this period the cover was not replaced; but as it subsided the pot was again covered with the iron plate, until it was necessary to remove it for the introduction of more sulphide. For thirty-six hours after the last portion was added the same steady heat was continued, and the contents of the pot occasionally stirred by means of an iron rod which passed through the top of the lid. During this period also the workman tested from time to time the security of the process, by cautiously removing the pots, and observing to what height the flame then rose, and with what vigour it burnt. The proper temperature was indicated by a vigorous combustion, accompanied by a flame which did not rise more than 3 or 4 inches over the edge of the pot.

When the thirty-six hours were expired the whole was allowed to cool, after which the pots were removed and broken, and the vermilion which was incrusted within them, and chiefly in their upper parts, collected, ground with water between horizontal stones, then passed through sieves, and thereafter elutriated and dried. The usual loss in converting the black sulphide by this process into vermilion was nearly 3 per cent.

Method adopted at Idria.—At Idria, as already stated, large quantities of the sulphide of mercury pigment are annually prepared. The method pursued is to introduce into a number of well-bound casks, contrived to turn on their axes, 8 lbs. of sulphur and 42 of mercury, and then to put them in motion for three hours or more, till the ingredients combine to form a brownish powder. A number of cast-iron cylinders placed upright in a furnace, and heated to dull redness, are then charged with this product, 100 lbs. being portioned to each, the weighted cast-iron cover being immediately fixed on, and retained till all crackling noise subsides. When this happens the iron top is removed, and another of stoneware, having the beak connected with a tube and receiver, substituted; at the same time the fire is increased for the purpose of expelling the sulphide of mercury from the iron cylinder. After the sublimation of the charge the capital and tube are removed, and when cold the cake of cinnabar is separated. That which has the brightest tint is found caked on the outside of the cover; the portion collected in the tube and receiver is generally mixed with an excess of sulphur, which volatilizes with it, and for the most part is returned with a fresh charge of æthiops to be re-sublimed. The cakes of cinnabar are broken, and ground finely with water; then boiled with a solution of potash, washed first with hot, next with cold water, and finally dried.

Chinese Vermilion, which is so rich in colour as to

command five or six times the price of the European product, appears to be prepared in the ordinary way, leaving nothing to account for the superior brilliancy of shade except the sunnier climate. By careful selection the finest portions are collected, and, if necessary, ground and washed several times. In making the artificial product 1 part of sulphur and 4 of mercury are introduced into an earthen pot, to which an iron cover is luted and bound with wire; the pot with its contents is then placed in a fire of dried camel's dung. After sublimation the cover is removed and the pot broken, and the purest of the sublimate picked out from the less-coloured product, ground very fine, and the powder sifted into a large vessel of water. When the red product has subsided the supernatant water and scum are drawn off, and fresh liquid supplied, in which the sediment is stirred up, and after subsidence the substance is collected and carefully dried in the sun.

By subliming one part of antimonious sulphide, Sb_2S_3, with mercuric sulphide, a greyish cinnabar is obtained. On boiling this with a solution of *liver of sulphur*—a compound of sulphur and potassium—and afterwards with hydrochloric acid, and washing thoroughly with water, a product is obtained which is quite as brilliant as the finest Chinese vermilion, and retains no antimonial sulphide.

Properties.—Sulphide of mercury, prepared by saturating a solution of oxide of mercury, is a black substance; but when prepared by the other processes mentioned it has a red colour, more or less lively. It is a soft, heavy, colourless, and tasteless powder if prepared by the moist method, and is devoid of crystalline structure; but the sublimed product appears in masses composed of hexahedral needles. Exposed to the light of the sun it gradually acquires on the surface a grey tint, owing to a portion being decomposed into mercury and sulphur.

Water or alcohol have no action upon cinnabar. Cold hydrochloric and nitric acid singly fail to dissolve it; but nitro-hydrochloric acid readily attacks it, and converts it into chloride. Nitric acid when heated decomposes it, and produces mercuric sulphate. Caustic potash, or soda in solution, does not decompose cinnabar; but if the hydrate of the alkali be employed, and its action be assisted by increased temperature, decomposition takes place, which results in the production of metallic mercury, sulphate and sulphide of the alkali.

A temperature approaching a red heat volatilizes mercuric sulphide without decomposition; if air be admitted the sulphide burns, the sulphur being converted into sulphurous and sulphuric acids, and the metal disseminated in the vapour. Charcoal and other carbonaceous matters, iron filings, lime, or any of the fixed alkaline bases, also abstract the sulphur and set the metal free.

Cinnabar or vermilion is principally employed as a pigment. Its high price exposes it to considerable sophistication in the hands of unprincipled traders. The adulterations which are most likely to be contained in it are minium or red lead, ferric oxide, red brick dust, and arsenious sulphide, AsS_3. Red lead, brickdust, or ferric oxide, may be readily found by sublimation of the mercurial sulphide containing them in a clean iron spoon. The difference of weight before and after treatment indicates the amount of adulteration. Sulphide of arsenic may be found by treating the pigment repeatedly with strong solution of potash, boiling, filtering off the liquid, adding to it hydrochloric acid with a few fragments of zinc or iron, and subsequently transmitting sulphuretted hydrogen gas through the solution, then boiling, filtering off the liquid, and adding hydrochloric acid to it to saturation. After some time sulphide of arsenic of a yellow colour falls.

The quantity of arsenic may be ascertained by the following process:—Take a given weight of the vermilion in very fine powder, put it into a flask, and treat it therein with *aqua regia* until the sulphur which separates has agglomerated into yellow lumps of a perfect yellow colour; fresh portions of *aqua regia* being added from time to time, in order to insure complete decomposition. The solution is filtered, and saturated with ammonia; an excess of ammonium sulphide is then added, the flask is loosely corked up, and the whole is left to digest in a warm place for ten to twelve hours. The flask is then allowed to cool, and the insoluble mercuric sulphide separated by filtration. The filtrate, which contains the sulphide of arsenic, should be diluted with a large quantity of water, acidified with a little hydrochloric or acetic acid until it is slightly acid, and the whole left to digest at a gentle heat until all odour of sulphuretted hydrogen has disappeared. The sulphide of arsenic which was held in solution will then have completely precipitated; it should be collected on a counterpoised filter, and weighed.

The presence of *red lead* may be detected by boiling the suspected vermilion in acetic acid, which will dissolve the lead if present. If, on passing a current of sulphuretted hydrogen through a portion of the filtered solution, a black precipitate of sulphide of lead is obtained, or if, on testing another portion of the filtered solution with iodide of potassium, a yellow precipitate is formed, lead is present.

In order to determine the quantity of the red lead, the black precipitate of sulphide of lead produced in the acetic acid solution above-mentioned is treated with hydrochloric acid, which produces an evolution of sulphuretted hydrogen; nitric acid is then added, and the whole evaporated to dryness. Sulphuric acid is now poured with care on the dry mass, the excess of sulphuric acid driven off by heat, and the remaining sulphate of lead weighed.

Chlorides of Mercury.—Of all the compounds of mercury, none are of greater importance, in a medicinal point of view, than the two compounds produced by the union of chlorine and mercury, and which are well known by the title of *calomel* (subchloride of mercury, mercurous chloride, Hg_2Cl_2) and *corrosive sublimate* (mercuric chloride, $HgCl_2$).

Calomel (*Mercurous Chloride*, Hg_2Cl_2).—As stated under the ores of mercury, this combination is met with in several mines in the form of incrustations—horn quicksilver—on other ores, or disseminated in

the form of small transparent and translucent crystals. Those mines where it is particularly noticed are the Almaden, Idria, Moschellandsberg; the mines of the Palatinate, Deux Ponts, and Bohemia. The quantity so found is, however, unimportant; and the native substance is never applied in medicine, that which is artificially prepared being preferred. There are several methods by which mercurous chloride may be obtained, as well by precipitation as by the dry way. When a solution of pure subnitrate of mercury is precipitated by another of a pure alkaline chloride, such as sodium chloride, or with dilute hydrochloric acid, a white flocculent mass falls, which is the compound in question; and when washed well and dried, it is chemically pure. It is necessary, however, to prolong the washings, otherwise some traces of the alkaline precipitant are retained, which react as a solvent upon a part of the precipitate by forming a double compound with it; and hence it is that calomel prepared in this way always leaves a mercurial taste. To guard against this, recourse is usually had to the dry method, in which the mercurous salt and chloride of sodium are mixed in the proper proportions, and then submitted to heat in a subliming pot, when the calomel is obtained in the form of a white incrustation on the cover of the vessel. Prepared in either way, mercurous chloride is a yellowish-white powder, which under the influence of solar light turns grey, being transformed into mercuric chloride and metallic mercury; it is but very slightly soluble, 1 part of the salt requiring 12,000 of boiling water for perfect solution. Dilute hydrochloric acid has no action upon it; but when concentrated, it changes the salt into metal and mercuric chloride.

Concentrated boiling solutions of the fixed alkaline chlorides, and of chloride of ammonium, react upon calomel in the same way. Hot strong nitric acid readily dissolves the subchloride of mercury, converting it into mercuric nitrate and chloride. It is readily sublimed, and forms crystals on condensing.

Although CHRISTISON and other authorities assert that the calomel prepared by precipitating a dilute solution of a mercurous salt with one of chloride of sodium in the manner already stated, or by agitating a solution of ferric chloride with metallic mercury, does not differ in therapeutic properties from that formed by sublimation, still the latter method is adopted in the manufacture.

Various recipes are known for obtaining it; thus, by mixing 4 parts of corrosive sublimate (mercuric chloride) with 3 parts of the metal, and subliming, calomel is obtained; likewise when mercuric sulphate of the protoxide of this metal is heated with an equivalent proportion of common salt and mercury, corrosive sublimate is produced. In the first instance the reaction may be symbolized thus—

Mercuric chloride. Mercury. Mercurous chloride.

$$HgCl_2 + Hg = Hg_2Cl_2$$

and in the second,

Mercuric sulphate. Mercury. Sodium chloride.

$$HgSO_4 + Hg + 2NaCl =$$

Mercurous chloride. Sodium sulphate.

$$Hg_2Cl_2 + Na_2SO_4$$

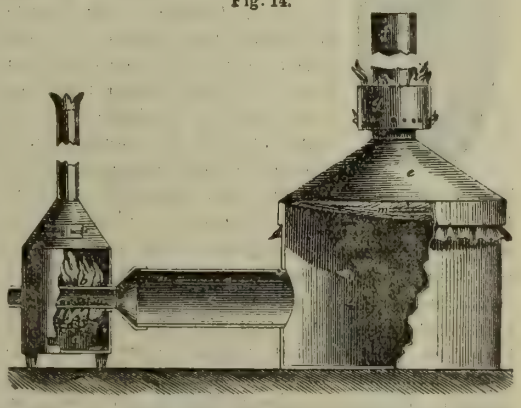
When operating according to the first equation, it is requisite to have the metal in slight excess in order to insure the complete reduction of the mercuric chloride. MOHR states that this method is frequently adopted in the German pharmaceutical laboratories. The materials are ground up with a little water or spirit, to prevent the escape of dust or powder, and when the metal is *deadened* the material is placed in glass vials and heated; after sublimation the product is collected by breaking off the neck of the bottles, and detaching the crust of salt.

When preparing it by the second method, which is much the better of the two, 2 parts of mercury are dissolved in 3 of strong sulphuric acid; or better still, 4 ounces of the metal are acted upon with 2 ounces 2 drachms, liquid measure, of strong sulphuric acid, to which half a fluid drachm of strong nitric acid is added.

When sulphuric acid only is employed, the sulphate of mercury obtained by evaporation is mixed with 2 parts of metal, and afterwards with 1½ part of common salt, the whole being triturated in a mortar till the metal disappears. The mass is then sublimed in the usual way. In this operation the whole of the mercury is, however, never reduced to calomel, and on this account the sublimed mass requires purification from corrosive sublimate by repeated washings with boiling water, in which the latter is freely soluble. As soon as the washings give but faint indications of precipitates with a solution of nitrate of silver or hydrogen, the calomel may be considered pure.

Fig. 14 is a drawing of a subliming apparatus described by MOHR. It consists of an earthenware tube, *b*, 1 foot long and a little more than 2 inches wide. This tube passes through a small furnace, and is connected on the left with a small bellows,

Fig. 14.



and on the right with the wider pipe, *c*, that enters the box or chamber, *d*, where the sublimed calomel collects. This box is lined inside with glazed paper, the top being secured by a cloth, *m*, which is retained in its place by the funnel-cap, *e*, terminating in the chimney, *f*. At *g* is shown a small iron gallery for

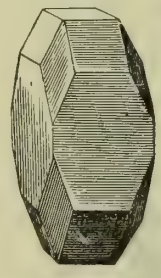
retaining hot charcoal, by which means a continuous draught is maintained.

The fire is laid on at *a* and *g*, and as soon as the temperature rises to the subliming degree, air is urged through the apparatus by working the bellows, and this forces the calomel vapour, as fast as it rises, into the chamber, *d*; as soon, however, as the chimney has become sufficiently hot the blowing apparatus may be detached, as there will then be sufficient draught to carry the sublimed vapour into the receiver without mechanical aid. As the charge already in the tube, *b*, becomes exhausted, a further quantity may be introduced at the open side, and as long as the fire in *g* remains, the current of air drawn through will be sufficient to prevent any mercurial vapour escaping by the open end.

Under ordinary circumstances the incrusted calomel requires to be finely ground before it is fit for use. This operation is generally performed under lead rollers, unless the salt be minutely subdivided at the moment of condensation. Mr. JEWELL patented a process for effecting this, which has since been improved by M. O. HENRY and SOUBEIRAN. It depends on the fact that if the mercurial vapour is made to pass into a vessel charged with steam, having water in the bottom instead of the air chamber, the substance becomes reduced to the finest state of division without further trouble.

Properties of Calomel.—The form in which calomel sublimes is modified by the dimensions of the apparatus employed, and the temperature at which it is produced. Prepared in small vessels, it usually takes the shape of a fibro-crystalline cake, which when powdered is yellow or buff; whereas if the apparatus is large, and the receiver cold, it falls as a white impalpable powder. The crystals of calomel are square prisms (Fig. 15), with a specific gravity of 7·150; 7·156, PELOUZE and FREMY; 6·9920, KARSTEN. Calomel is not volatile at ordinary temperatures. Below a red heat it sublimes without fusing. It has neither taste nor smell, and is insoluble in pure water at 15°·5 C. Boiling muriatic acid quickly changes calomel into corrosive sublimate and metallic mercury. In hot nitric acid it dissolves, evolving nitric oxide. In the cold, sulphuric acid neither dissolves nor decomposes it; but the action of hot sulphuric acid is to produce—the higher chloride, a mercuric sulphate, and sulphurous acid gas. Solutions of the fixed alkalies convert it into black oxide; and by ammonia gas, dry mercurous chloride becomes mercurosammonium chloride, $HgNH_3Cl$, which is also black. This compound is different from that which is formed when calomel and aqueous ammonia are brought in contact; the last has the formula, Hg_2NH_2Cl, dimercurosammonium chloride. The equation is as follows:—

Fig. 15.



Mercurous chloride.		Ammonia.		Dimercurosammonium chloride.		Ammonium chloride.
Hg_2Cl_2	+	$2NH_3$	=	Hg_2NH_2Cl	+	NH_4Cl.

The trade adulterations of calomel are chalk. sulphate of baryta, carbonate of lead, common salt, sal ammoniac, and sometimes a little corrosive sublimate. For the detection of all impurities, the Edinburgh College directs that heat, sulphuric ether, and solution of caustic potash should be employed. Calomel, if pure, is entirely volatilized by heat; all fixed impurities will therefore be found in the residue, whilst the sublimate may contain, besides calomel, the mercuric chloride and sal ammoniac. These impurities being soluble in water, a solution is readily obtained containing both; and this liquid, when acted on by potash solution, gives a yellow precipitate or cloud, after which, if gently heated, fumes of ammonia will be given off, producing, in contact with muriatic acid, the white vapours of ammonium chloride. Or the liquid may be gently evaporated, and the solid residue treated with solution of caustic potash, after which the volatile ammonia may also be brought in contact with the hydrochloric acid vapour.

The fixed residue, supposed to contain barium sulphate, white lead, and chalk, may now be treated with pure and dilute nitric acid; any insoluble matter still remaining is set aside for examination, and the solution in nitric acid, which, if it was attended with effervescence, showed the presence of carbonic acid, may be if necessary diluted with water. Solution of sulphuretted hydrogen gas is then added, and a black precipitate obtained, if lead be present. The clear liquid filtered from the plumbic sulphide is next neutralized by ammonia, and ammonium oxalate added. A white precipitate proves the presence of lime.

Returning now to the insoluble residue from the nitric solution, which may still contain plumbic sulphate and barium sulphate, the solid matter may at once be tested with a drop of sulphide of ammonium. It lead be present, it will be immediately blackened. If otherwise, then, having been well washed with water, it may be boiled with pure potassium carbonate, the solution filtered, excess of alkaline carbonate in the liquid expelled by pure hydrochloric acid, and afterwards barium chloride added to detect the presence of sulphuric acid. If a white precipitate is observed, then the white matter left on the filter is carefully washed and dissolved in a small portion of pure hydrochloric acid; to this liquid dilute sulphuric acid is next added, and a precipitate of barium sulphate is obtained.

It is well known that calomel boiled with water, very slightly acidulated with hydrochloric acid, and containing a slip of clean copper, gives a deposit on that metal of metallic mercury. In the case of a solution of corrosive sublimate, the same test may be employed, or the following neat arrangement may be adopted:—A drop of the liquid is placed on a sovereign, and an iron key is placed so that one part is immersed in the liquid whilst another touches

the gold of the coin. At the former point a brilliant mercurial stain is immediately produced by the galvanic current. A copper coin may take the place of the gold, in which case a strip of clean zinc, slightly arched, must be substituted for the iron key.

Finally, it being established that the solution contains mercury, the identification of it, as the mercurous chloride, may be easily effected by solutions of nitrate of silver, caustic ammonia, iodide of potassium, and stannous chloride.

Medicinally, calomel is the mildest and most generally employed of all mercurials. It is irritant, however, in large doses, and to some constitutions violently so. Combined with digitalis or squills it is an effective diuretic; and its diaphoretic, like its sedative properties, are best developed in combination with opium. Its alterative properties are most generally produced by the use of small doses daily, or it may be given along with the golden sulphide of antimony, as *Plummer's pill*.

The Editor trusts, however, that before many years are over medical men will have abolished the administration of all hydrargic compounds, which can only have a baneful effect upon the system.

Corrosive Sublimate (*Mercuric Chloride*, $HgCl_2$)—This combination of mercury has been known from time immemorial, though the first description of it was given by Geber, of Thus, in Persia, who lived in the ninth century; and it has occupied ever since a prominent place in the *materia medica* of succeeding physicians. It may be prepared by acting upon mercuric sulphate by various metallic chlorides in solution—chloride of barium, for instance—when a mercuric chloride is produced, together with a sulphate of the precipitant. If the latter be insoluble, as in the case of barium, the mercuric chloride may be obtained by evaporating the filtered liquor to dryness. Alkaline chlorides, magnesium chloride, and other similar salts, effect the same changes, but slowly. By bringing together the vapour of mercury and chlorine gas in the equivalent proportions, the metal takes fire and burns, forming $HgCl_2$.

None of these methods are, however, followed in its manufacture, recourse being always had to the dry process of subliming a mixture of chloride of sodium and mercuric sulphate, when a chloride of the latter and sulphate of sodium are formed, the mercuric chloride compound being expelled by the heat. Thus:—

Mercuric sulphate.		Sodium chloride.		Mercuric chloride.		Sodium sulphate.
$HgSO_4$	+	$2NaCl$	=	$HgCl_2$	+	Na_2SO_4

Considerable quantities of this compound were prepared by the Dutch manufacturers before the knowledge of its formation became more general. Their mode of procedure was to mix equal parts of mercuric nitrate, chloride of sodium, and calcined ferrous sulphate, and introduce the composition into a matrass, filling only one-third its capacity. The vessel was then imbedded in a sand bath, and heat applied till its bottom assumed a dull red, when a series of decompositions took place, by which a mercuric chloride was produced and sublimed, whilst sodium sulphate and ferric oxide remained in the matrass, and the nitric acid, after suffering decomposition, was evolved together with oxygen. Another process was to cause metallic mercury, chloride of sodium, saltpetre, potassium nitrate, and calcined ferrous sulphate to react upon one another in the matrass by heat, when corrosive sublimate resulted.

Kunkel improved upon the process by producing first mercuric sulphate, by acting on the metal with oil of vitriol; and heating in a matrass equal parts of this and common salt. Subsequently, Fourcroy, in order to dispense with the first operation, directed to employ sulphuric acid, mercury, and common salt, to submit the mass to heat, and finally to sublime it. In practice the proportions taken were 10 parts of mercury, 8 of common salt, 11 of sulphuric acid, 6 of peroxide of manganese, and 3 of water.

The London College directs that 1 lb. of mercury be boiled with 31 fluid ounces of sulphuric acid, and that the dry sulphate is to be mixed with half a lb. of salt, and sublimed.

In the receipt of the Edinburgh College the process for preparing calomel and corrosive sublimate is the same, with the exception that only half the quantity of mercury is taken for the latter.

The Dublin College first prepares mercuric sulphate, and intimately mixes this in fine powder with dried common salt, likewise ground, in the proportion of 2 of the former to 1 of the latter, subjecting the mixture to heat in an iron pot lined with clay, to which an earthen head is adapted. In either of these operations the temperature at which the salt is sublimed should not be too elevated, as in this case the chloride would fuse and fall back into the vessel, and thus occasion a loss.

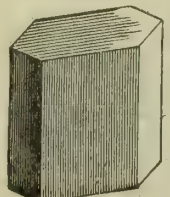
In the formation of the mercuric sulphate, preparatory to subliming it with common salt, the materials are introduced into a cast-iron boiler, placed in brickwork, having a fire beneath it, and surmounted by a hood to carry off the noxious gas evolved into the chimney. The heat required to effect the union of the mercury with the acid is moderate. The mass forms a thick magma, and continues to evolve sulphurous acid as long as any metal remains unoxidised. Some mercurous sulphate (Hg_2SO_4) is apt to be produced; but as it is necessary for the purity of the chloride which is intended to be obtained from this, to have the whole of the metal in the state of mercuric sulphate, a quantity of acid should be employed at the end of the process, before the drying of the salt. The better to insure this, tests may be made with a portion of the sulphate from time to time, by suspending it in water saturated with chloride of sodium; when the whole dissolves, it is evident that all the mercury is in the form of mercuric sulphate; but should a white deposit be formed, it indicates that mercurous sulphate still remains. When the sulphate is prepared it is mixed with the requisite quantity of alkaline chloride, and a little binoxide of manganese—1 part to 10 of the mercuric sulphate operated upon—and allowed to remain during two or three days, with the

view of effecting a thorough decomposition. At the expiration of this period the fire is lighted, and a gentle heat maintained till all moisture has evaporated; after which the mass is put into the sublimers, which may be of green glass, resting on cast-iron plates, and imbedded in sand up to the neck. In large factories the subliming furnace is usually an oblong, capable of holding about 100 matrasses, and heated by fires symmetrically disposed along the longer side. These are generally covered by a prismatic conical hood, from which a pipe leads into the chimney to carry off any escaping vapour of the mercurial compound. The most important part of the business is the regulation of the heat, which, in the first instance, disengages moisture, and after this the mercurial salt. At this stage a small glazed conical vase is inverted on the neck of each matrass. When white vapours are observed it is a certain sign that the heat is too strong, in which case the vessel must be cooled by removing a portion of the sand from its upper part. Towards the end of the sublimation the blast must be increased, with the view of bringing the sublimed chloride nearly to its fusing point, for the purpose of causing it to adhere together in a compact cake; but, for reasons already assigned, the temperature must not be carried too far, since this would occasion a loss. After the sublimation the fire is withdrawn, and as soon as the sand has sufficiently cooled the matrasses are taken out, and broken in the middle as gently as possible, so as not to detach the crust of salt upon the upper part. Finally, the fragments of glass, &c., are removed, and the pure cakes set aside to be ground and packed.

Any mercurous chloride which may happen to be formed during the sublimation, owing to its not being so volatile as corrosive sublimate, forms a whitish ring on the lower part of the sublimed crust, and thus admits of being removed. Such portions may be added in the succeeding charge which is being converted into sulphate, and afterwards re-sublimed.

Properties.—Ordinary sublimed mercuric chloride is a white satiny substance having a crystalline appearance, although often no distinct order can be distinguished. If, however, the sublimation be effected at a low heat, and as slowly as possible, crystals appear having the shape of flattened tetrahedral prisms, Fig. 16, with a specific gravity of 5·4. The sublimed salt appears more or less translucent, and when in thin fragments often transparent. In the heat it is very volatile, entering first into fusion before it is disseminated. It melts at 265° C., boils at 295° C., and, according to Faraday, volatilizes at ordinary temperatures. Water dissolves it very readily; 16 parts are required in the cold, but 3 parts at 100° C. are sufficient to dissolve 1 part of it, and the liquid reacts acid to test-paper. A hot, concentrated, aqueous solution of mercurial chloride deposits crystals on cooling, which slightly differ in appearance from those obtained by sublimation; they are anhydrous. Alcohol and ether also take it up very freely; 7 parts of cold alcohol dissolve 3 of corrosive sublimate, but the same quantity at a boiling temperature takes up 6 parts of the salt. When sulphuric ether is added to a solution of corrosive sublimate in water the mobile liquid abstracts the salt, and an ethereal solution of chloride of mercury floats on the water, which is more or less reduced of its saline constituent. Acids aid in the solution of this body in water, without, however, causing any decomposition or alteration of it. By exposure to sunlight an aqueous solution of the salt suffers decomposition into calomel, hydrochloric acid, and oxygen, thus:—

Fig. 16.



Mercuric chloride.		Water.		Mercurous chloride.		Hydrochloric acid.		Oxygen.
$2HgCl_2$	+	H_2O	=	Hg_2Cl_2	+	2HCl	+	O.

It is likewise decomposed by various substances, metallic, non-metallic, and organic; the latter usually converting it to the state of mercurous chloride. It forms insoluble, or at least but very partially soluble, precipitates with albumen and fibrin.

On all animals the effects of chloride of mercury are, as its technical name implies, those of a corrosive poison, and it has proved fatal to man by even its external application. When swallowed in any quantity, the symptoms come on almost immediately. Indeed, the rapidity of their appearance and the strong metallic taste which is experienced, are among the phenomena which strongly distinguish cases of poisoning by this agent from those occasioned by arsenic. The best antidote against its poisonous action is the white of egg suspended in water and milk—one egg is said to be required for every *four grains* of the poison; hydrated sesquioxide of iron has also been recommended, and likewise, on account of the gluten it contains, wheat-flour and water.

This salt has been extensively employed for the preservation of subjects of natural history, and likewise for preserving wood against the dry rot.

Mercuro-diammonium Chloride.—Fusible White Precipitate, $HgN_2H_6Cl_2$.—This compound is obtained by dropping a solution of mercuric chloride into a boiling solution of sal-ammoniac containing free ammonia, as long as the precipitate which forms is redissolved on shaking. On cooling the liquid, the salt separates in regular dodecahedrons.

It is also produced by adding potash to ammoniomercuric chloride ($(NH_4Cl)_2HgCl_2$) in solution.

Mercurammonium Chloride, Infusible White Precipitate, is formed by adding ammonia to a solution of mercuric chloride in a large quantity of water.

For a long time this body was thought to be identical with calomel, till Rammelsberg showed it to be different, and Kane demonstrated its true composition in his researches on the *Amides*.

Mercurammonium chloride is a snow-white salt without odour, but possessing a nauseous metallic taste. It requires for solution about 600 parts of water, but the mineral acids readily dissolve it. When heated it volatilizes without fusing.

When the precipitate is boiled in water, chloride of ammonium is produced, and a heavy yellow powder falls. Potash likewise changes it into oxide and chloride of the metal, ammonia being evolved. Caustic ammonia has no apparent action, and hence this alkali serves to distinguish it from calomel, which is turned grey or blackish by it.

In cases of poisoning with white precipitate, albuminous antidotes, such as are given to reduce the action of corrosive sublimate, serve best.

It is said that white precipitate is much adulterated with sulphate of lime, carbonate of lime, and carbonate of lead. The extent of the adulteration may readily be found by heating a weighed quantity, and weighing the residue, should any be left.

Mercuric Fulminate; Fulminating Mercury.—*Mercure fulminante*, French; *Knallquecksilber*, German. Formula, $Hg_2C_2N_2O_2$.

This very explosive compound was first described by HOWARD in the Philosophical Transactions for 1800. It is a compound of mercury with fulminic acid ($C_2N_2H_2O_2$), a body polymeric with cyanic acid (CNHO) and cyanuric acid ($C_3N_3H_3O_3$). Fulminic acid is formed in a peculiar reaction of nitric acid and alcohol in the presence of a silver or mercury salt.

Mercuric fulminate should be made in successive small quantities: 100 grains of mercury are treated with 1½ ounce by measure of nitric acid, aided by heat in a porcelain basin, till the whole is dissolved. As soon as the liquid is cold, 2 ounces by measure of alcohol, specific gravity ·85, are added, and a gentle heat applied. Brisk action takes place, carbonic acid, nitrogen, and red vapours being copiously evolved, and a yellow-grey precipitate deposited, which is the compound in question. If the effervescence be too brisk, the vessel should be withdrawn from the heat, and its contents cooled by the addition of more alcohol. As soon as the precipitate has formed, it is to be well washed by decantation and filtration, only a small quantity of distilled water being used in the latter process. The temperature at which the compound is dried should not exceed 100° Fahr., and only small quantities should be operated upon at a time to guard against an explosion: 120 grains of the fulminate are obtained from the above quantity of mercury when the operations are successfully conducted. It happens that on the addition of the alcohol, a portion of the mercuric salt is reduced to the state of metal, but this can be separated from the yellowish salt after the spirit is decanted by treating with boiling water, in which the fulminate is soluble; and by filtering off the liquor and setting it aside to cool, the salt separates in silky acicular crystals. When it is required to prepare it in large quantities, the course followed is to dissolve 1 part of mercury in 12 of nitric acid of 1·36 specific gravity, and to add 11 parts of alcohol, specific gravity ·850, when the solution is cold. On slightly heating the vessel, brisk action takes place as above stated, and similar effects are produced. The separated metal is removed from the explosive compound by boiling water, from which the fulminate is deposited on cooling in silky crystals. CRE-MASCOLI directs, as the safest method, to treat half an ounce of the metal with 6 ounces of nitric acid of 1·30 in a flask, which should be held in boiling water for a minute or so, and as soon as solution takes place, and the temperature is reduced to 55° Fahr., to pour in 4 ounces of alcohol of ·833 specific gravity, and again to immerse the flask in boiling water for two or three minutes, till dense white fumes begin to fill the upper part of the vessel, at which period it should be removed from the heat. The reaction is said to be very moderate in this instance, and the whole of the fulminate falls down in the course of a few hours, when it may be purified by decantation and washing.

Fulminate of mercury is an extremely dangerous substance to operate upon, owing to the readiness with which it explodes; the violence of its explosion has repeatedly been the cause of serious injury, and even of loss of life. It detonates strongly when struck with a hard body; but sometimes trifling friction may serve to produce this effect, even when in a moist state. Heated to 300° Fahr. it explodes, and at the same time evolves a bright flame; the electric spark and contact with strong nitric and sulphuric acids, also induce its decomposition, which is invariably accompanied with explosion. The products resulting from it, when detonated, are carbonic acid, nitrogen, and vapour of mercury.

Fulminating mercury is principally used for the manufacture of percussion caps. To fill the caps it may be moistened with a little resinous tincture, and dropped into the little capsule, but the almost universal practice is to mix it with about 6 per cent. of nitrate of potash and water, sufficient to reduce the whole to a thin paste. A small quantity of this is dropped into each cap, and carefully dried at a low heat.

MOLYBDENUM.—*Molybdène*, French; *Molybdän*, German. Symbol, Mo. Atomic weight, 96.—This metal occurs only in small quantities, and has not as yet been made use of in the arts. It is found as a sulphide (*molybdenite*, molybdänglanz, wasserblei, MoS_2), as lead molybdate (*wulfenite*), and as a trioxide (MoO_3, *molybdic ochre*, or *molybdin*).

Molybdenum forms three oxides—molybdous oxide, MoO; molybdic oxide, MoO_2; trioxide, or molybdic anhydride (molybdic acid), MoO_3.

The first two oxides are formed by reduction of the trioxide. Molybdic anhydride is produced by roasting the sulphide with constant stirring, in an open crucible, or by fusing the sulphide with nitre.

Native lead molybdate is digested in dilute hydrochloric acid to remove the zinc, iron, and cadmium; and is then heated with 1¼ part of strong sulphuric acid, with constant stirring. The solution is allowed to cool, abundance of water added, and the insoluble lead sulphate filtered off. The filtrate is then treated with nitric acid, and evaporated, with constant stirring, in a porcelain vessel till the acid begins to be volatilized; the trioxide of molybdenum then separates as a white powder.

Molybdenum Blue is formed by reduction of the

trioxide by a quantity of sulphuretted hydrogen insufficient to produce sulphide, in presence of water, followed by heating to precipitate the sulphur. On boiling the trioxide with hydrochloric acid, chlorine is evolved, and the blue oxide of molybdenum formed. Treatment with stannous chloride also produces the colour, with formation of stannic chloride.

Molybdenum sulphide was discovered by SCHEELE in 1778. The metal was first isolated by HJELM in 1782. Metallic molybdenum is prepared by heating a mixture of the trioxide with 1½ part of potassium cyanide to a white heat in a luted porcelain crucible, inclosed in a larger crucible filled with charcoal (J. E. LOUGHLIN). The reduction of any of the oxides of molybdenum may be effected by heating them to a full white heat in a charcoal-lined crucible, or with carbonate of soda on charcoal before the blowpipe (BERZELIUS). Molybdic anhydride or the lower oxides are also reduced to the metallic state if heated to whiteness in a current of dry hydrogen gas (BERZELIUS).

Molybdenum is a white silvery metal, harder than topaz, and requiring an extremely high temperature for its fusion; its specific gravity is 8·6. The pulverulent metal obtained by reduction with hydrogen oxidises in the air and takes fire when heated; but the buttons of metal obtained by fusing it in DEVILLE'S blast furnace do not oxidise at common temperatures.

The native sulphide (molybdenite) is very widely distributed, and if sought for would probably be found in sufficient quantity to be used for manufacturing purposes. It closely resembles plumbago in appearance, and was long mistaken for it. The mineral has a pure lead-grey colour, and gives a grey streak on paper. It is found in Cornwall, Cumberland, Saxony, Bohemia, Sweden, Greenland, the United States, &c.

NICKEL.—English, French, German. Symbol, Ni. Atomic weight, 58·70.—This metal was discovered by CRONSTEDT in 1751. Its principal ore is an arsenide, NiAs, a copper-coloured mineral, called by the German miners *kupfer-nickel*, or dirty copper, because they were unable to extract copper from it. This ore was analyzed by CRONSTEDT, and having isolated the metal, he gave it the name by which the miners had stigmatized the ore.

Nickel may be obtained pure on a small scale by several processes. The kupfer-nickel is roasted to remove the arsenic and oxidise the nickel, at first alone, and subsequently together with charcoal dust; and this roasting must be continued till no vapours of arsenic are given off.

The roasted ore is then dissolved in nitric acid or *aqua regia*, and the solution evaporated to expel excess of acid. A large quantity of water is now added, and sulphuretted hydrogen passed through the liquid till all the arsenic, copper, bismuth, and antimony are precipitated. The iron, cobalt, and nickel are precipitated from the filtrate with carbonate of soda; and the precipitate, after being well washed, is treated first with oxalic acid, and then with ammonia, the solution of the nickel oxalate in aqueous ammonia being repeated till the liquid no longer contains cobalt. Potash solution is then added, when a pale green precipitate falls, consisting of hydrate of nickel, NiHO. After washing and drying, this precipitate is introduced, either alone or made up into a paste with oil, into a charcoal-lined crucible, and subjected to the heat of a blast furnace, when a well-fused button of the metal is soon formed.

The metal may also be obtained by heating the nickel oxalate in a crucible with a luted cover, without any other reducing agent than the carbonic oxide furnished by the decomposition of the acid.

Pure nickel is a brilliant, silver white, ductile metal, little more fusible than iron. At ordinary temperatures it is susceptible of magnetism, but it loses this property almost entirely if heated, though it recovers its magnetic power on cooling. Nickel becomes oxidised by exposure to a current of air at an elevated heat. The metal is easily attacked by nitric acid and aqua regia, and is dissolved slowly with evolution of hydrogen in sulphuric or in hydrochloric acid. Its specific gravity is 8·82.

Sources.—Native nickel occurs at Westerwald in the Erzgebirge, in Bohemia, combined with arsenic, under the significant name of *kupfer-nickel;* with arsenic, cobalt, iron, and copper, as *arsenic-nickel*, in the Hartz; at Riechelsdorf in Hessia, as an oxide, in *nickelschwartze;* as a sulphide in *haarkies;* as a sulphide and arseniate of nickel in *nickelglanz;* and with sulphur and antimony in *nickelspeisglanzerz*, at Siegen, and near Freussberg, in the principality of Nassau. Nickel is always present in meteoric stones. Kupfer-nickel occurs in numerous external shapes, as uniform, globular, botryoidal, arborescent, massive, and disseminated; fracture, coarse or fine grey; in silver and cobalt veins, in gneiss, sienite, mica-slate, kupferschiefer, accompanied by speiss cobalt, native silver, quartz, &c. It is found in Westphalia near Ospe, in Hessia at Riechelsdorf, and Biber in Baden; in the Saxon Erzgebirge, near Schneeberg and Freiberg; in Bohemia, at Joachimsthal; in Thuringia, at Saalfeld; in Steyermark, near Schladming; in Hungary, France, and England.

Subjoined are the analyses and characteristic properties of a few of the more important of these minerals:—

Kupfer-nickel.—The composition of this mineral, as stated by STROMEYER and PFAFF, is as follows:—

		Riechelsdorf.
Nickel,	44·20	48·90
Arsenic,	54·70	48·70
Iron,	0·33	0·44
Lead,	0·32	0·96
Sulphur,	0·45	0·90
Loss,	—	0·10
	100·00	100·00

It is of a copper or yellowish-red hue, but acquires a grey or blackish tarnish by exposure. The specific gravity is 6·6 to 7·6. It occurs reticulated, dendritic, and botryoidal, but more commonly massive; never crystallized; streak, pale brownish-black. The frac-

ture is imperfectly conchoidal, or fine-grained and uneven, with a glistening or shining metallic lustre; it yields to the knife with difficulty, and is brittle. Before the blowpipe it gives out an arsenical vapour, and then fuses, though not very easily, into a white metallic globule. After roasting it usually tinges blue a bead of borax, indicating the presence of a certain quantity of cobalt. In nitric acid it assumes a green coating, and in aqua regia is dissolved.

Haarkies—Sulphide of Nickel.—The following is Arfedson's analysis:—

Nickel,	64·76	65·74
Sulphur,	35·24	34·26
	100·00	100·00

With traces of cobalt and arsenic. Its specific gravity is 6·45.

It occurs in capillary and sometimes diverging filaments of a yellowish colour, inclining to steel grey. Primary form the cube; flexible; opaque, with a metallic lustre; not magnetic. Before the blowpipe on charcoal, with a good heat, it fuses into a globule which is metallic, malleable, and magnetic, and consists wholly of nickel; but in the open tube it exhales the smell of sulphurous acid. With nitric acid it forms a greenish solution.

Nickelspeisglanzerz.—This mineral is generally a combination of nickel, sulphur, and antimony, in the following proportions:—

Nickel,	27·36
Sulphur,	16·98
Antimony,	55·66
	100·00

Its specific gravity is 6·45 to 6·5, and its primary form a cube. It occurs in masses which have a granular composition, and possess a steel-grey or silver-white colour; lustre, metallic; cleavage, perfect parallel to the faces of the cube; brittle. Before the blowpipe it is partly volatilized, disengaging vapours of antimony and sometimes of arsenic, and ultimately melts into a metallic globule, which communicates a blue tinge to glass of borax. It is acted upon by nitric acid, forming an immediate precipitate, and imparting to the solution a greenish tinge.

Horbachite.—The nickel ores of Horbach, near St. Blasien in the Black Forest, have been analyzed by E. Knop. These ores are imbedded in the serpentized gneiss of the locality, inclosing here and there granular aggregations of iron glance. They consist of nickeliferous magnetic pyrites, having a magnetic action, a metallic aspect, a pinchbeck-brown colour, inclining to steel-grey, darker than that of true magnetic pyrites, and giving a black streak. Hardness between 4 and 5; specific gravity 4·43. Cleavage imperfect, and in one direction only.

Analysis of the ore, when freed from the accompanying copper pyrites and iron glance, gave as a mean:—

	Per Cent.
Sulphur,	45·87
Iron,	41·96
Nickel,	11·98

This composition agrees very nearly with the formula, Fe_4NiS_{15}. The ore may be regarded as an isomorphous mixture of the trisulphide of iron and nickel, $4FeS_3 + NiS_3$.

This composition has not hitherto been observed among native sulphides, all those previously known being either bisulphides, sulphides of lower degree, or compounds of these with bioxides. On the other hand, the composition of the Horbach ore is by no means constant, a specimen having been found of specific gravity 4·7, which contained 40·03 per cent. sulphur, 55·96 per cent. iron, and 3·86 nickel.

Horbachite, when subjected to lixiviation in contact with the air, becomes oxidised and partly converted into the sulphates of iron and nickel, which dissolve out. Knop suggests that this fact should be taken as a basis for a new mode of extracting nickel from the Horbach ores, in place of the present barbarous treatment in the dry way hitherto adopted, whereby enormous quantities of sulphurous acid are thrown off, causing great injury to the neighbouring forests.

Nickel Silicates.—Nickel has lately been found in New Caledonia, and the ores have very great value on account of the ease with which the pure metal can be obtained from them.

The nickeliferous ores of New Caledonia are free from sulphur and arsenic. They are hydrosilicates of magnesia and nickel. The iron found in them is not in combination, and appears to occur only in small veins and nodules. The average composition of the ores is stated by P. Christofle and H. Bouilhet ("Comptes Rendus," lxxxiii.) to be as follows:—

	Per Cent.
Water,	22
Silica,	38
Ferric oxide,	7
Nickel monoxide,	18
Magnesia,	15
	100

The metal extracted from these ores, whether by the dry or wet process, is of excellent quality. That obtained by the wet process flattens under the hammer without breaking.

When the ore was reduced by the wet process and melted, the metal contained—

	Per Cent.
Nickel,	97·75
Silicon,	0·54
Carbon,	1·25
Manganese,	0·36
	99·90

Reduced by a mixed wet and dry process and melted, the alloy consisted of—

	Per Cent.
Nickel,	98·00
Silicon,	0·13
Copper,	0·50
Iron,	1·60
	100·23

In the province of Malaga, Spain, a mineral has also been discovered in which the nickel occurs in

the form of silicate, as in the ore met with in New Caledonia.

The absence of arsenic and antimony in these ores allows the extraction of a very malleable and easily-wrought metal, much superior to the products of the German mines.

The working of this new ore has been recently commenced. The mineral contains about 9 per cent. of nickel, and no cobalt (Meissonier, "Comptes Rendus," lxxxiii.).

Manufacture.—The nickel of commerce is chiefly obtained from kupfer-nickel, nickeliferous pyrites, and from the speiss obtained as a secondary product in the treatment of nickeliferous ores of cobalt. The preparation of pure nickel from speiss is conducted in accordance with a method first proposed by Wöhler. The powdered speiss is roasted, first alone, and afterwards with the addition of powdered charcoal, to effect the separation of its arsenic. The residue obtained by this process is at present mixed with 3 parts of sulphur and 1 part of carbonate of potash, and then fused in a large earthen crucible. This product is next treated with warm water, by which the arsenic and sulphur associated with potassium are dissolved, while the nickel, in the form of sulphide, remains at the bottom of the vessel in which the operation has been conducted. When, as sometimes happens, from the employment of too high a temperature at the commencement of the roasting, the whole of its arsenic has not been expelled, the operation must be repeated on the residual sulphide thus obtained. As soon as entirely freed from arsenic, the sulphides are well washed with warm water, and then dissolved in sulphuric acid, to which a small quantity of nitric has been added; the precipitation of the lead, copper, and bismuth, which may be present, is determined by a current of sulphuretted hydrogen gas, and the metals which still remain in solution are afterwards precipitated by an alkaline carbonate. This deposit, after being well washed, is then treated with an excess of oxalic acid, which forms an insoluble oxalate of iron, and leaves behind an insoluble oxalate of the oxides of cobalt and nickel. These are then dissolved in ammonia, and treated as already described. The oxalate of nickel deposited from this solution is, after being carefully washed to remove any traces of the ammoniacal liquor, ignited in a close crucible, having an aperture in the lid for the escape of the evolved gases.

As the metal itself is now extensively used in alloys, of which German silver is one of the most important, and in electro-plating, great pains have been taken to procure it in a state of comparative purity, and several processes have been proposed. According to Louyet, the process by which nickel is extracted from speiss at Birmingham, on the large scale, is as follows:—The speiss is first fused with chalk and fluor spar, the metallic mass obtained is reduced to powder, and roasted for twelve hours to expel the arsenic; the residue is then dissolved in hydrochloric acid; the solution is diluted, and the iron sesquioxidised by the cautious addition of bleaching powder. Milk of lime is then carefully added so long as sesquioxide of iron falls, which carries down with it the last portions of arsenic. This precipitate is well washed, and the liquid, which contains all the cobalt and nickel, is treated with a current of sulphide of hydrogen; the sulphides of copper, bismuth, and lead are thus precipitated, and are thoroughly washed. The whole of the nickel and cobalt still remain in the liquid, which is again treated with bleaching powder: the cobalt is thus thrown down as sesquioxide; after which the total quantity of the nickel is separated from the solution in the form of hydrated oxide, by adding milk of lime as long as any precipitate is produced.

The precipitated nickel is reduced by charcoal by a cementation process. Cylindrical crucibles of fire-clay are set vertically in a furnace, so that the flames may have free access to every part of their exterior. The crucibles are open at the top; below the fire bars they terminate in funnel-shaped ends provided with openings for the withdrawal of the charge. The dried oxide is mixed with oil and made into small lumps: these are mixed with powdered charcoal, and thrown in at the top of the crucible. The carbonic oxide reduces the nickel oxide. The metal, in pulverulent condition, but retaining the forms of the lumps in which the oxide was introduced into the crucible, is withdrawn at the bottom of the vessel from time to time, a fresh charge being at the same time added at the top, so that the process is thus made continuous.

The metal is obtained in ingots by fusing the lumps in fire-clay crucibles in a blast-furnace.

Cast Nickel Plates.—Owing to the great increase of late years in the manufacture of nickel-plated goods, large plates of metallic nickel have been much wanted for the anodes of the galvanizing nickel-salt baths; but the extraordinary refractory nature of pure metallic nickel has been till lately a great hindrance to the making of large castings.

Borchert has, however, lately succeeded in casting nickel plates 18 inches long, 14 inches broad, and 1½ inch thick. The nickel used was Saxon würfel-nickel, of 98 to 99 per cent. strength, and was fused in crucibles in a simple brazier's furnace by a coke fire. The secret of success appears to lie in maintaining a continually increasing temperature. The fusion requires laborious attention, the metal not becoming liquid till after at least six hours' firing. As soon as it becomes fluid it must be cast without delay into the sand moulds, for as soon as the fire drops a little the nickel is liable to solidify again into a solid mass, in which case a renewed fusion in the same furnace is impossible.

Analysis.—For the separation of nickel and cobalt, the method recommended by Liebig is the best. The cobalt and nickel having been freed from all other substances except salts of potassium or sodium, are precipitated in the form of hydrated oxides, which, after partial washing from the adhering alkaline salts, are mixed with caustic potassium hydrate and a decided excess of hydrocyanic acid; the mixture is then boiled for ten minutes in order to expel the greater part of the excess of hydrocyanic acid, and

to convert the oxides into double cyanides of cobalt and nickel. If the solution be now boiled with very finely levigated mercuric oxide, the nickel salt is decomposed, hydrated oxide of nickel is precipitated, and mercuric cyanide is produced.

The cobalticyanide of potassium remains in solution, and may be filtered from the oxide of nickel, which requires to be carefully ignited in a platinum crucible till it ceases to lose weight. The cobalt may then be precipitated from the filtrate as a white mercurous cobalticyanide, by the addition of solution of mercurous nitrate; the precipitate is collected, dried, and ignited, when pure oxide of cobalt is left, which may be reduced to the metallic state in a current of hydrogen.

The solution of the oxides, which must be free from nitric acid, is, after previous neutralization of the free acid which may be present by ammonia, precipitated with sulphide of ammonium, and highly dilute hydrochloric acid, according to ROSÉ, or acetic acid—WACKENRODER—is then added. This serves to dissolve the sulphide of manganese and the sulphide of iron, whilst the sulphide of cobalt and the sulphide of nickel remain undissolved, though the latter less completely. The sulphides of the metals are reprecipitated from the filtrate by the addition of ammonia and sulphide of ammonium, and the precipitate is treated once more with dilute hydrochloric acid. The results are nearly accurate.

Analysis of Kupfer-nickel.—The purified mineral is treated with *aqua regia*. The sulphuric acid is precipitated by barium chloride, and the excess of barium being removed by sulphuric acid, the arsenic acid is converted into arsenious acid by boiling with sulphurous acid, and then precipitated by sulphuretted hydrogen. The sulphide of arsenic obtained is, after drying and weighing, decomposed by *aqua regia* to obtain the sulphur. The liquor freed from sulphide of arsenic is concentrated with the addition of nitric acid, and is precipitated by excess of ammonia: an abundant precipitate of ferric oxide is formed, which generally retains a little nickel. It is redissolved on the filter by hydrochloric acid, and the liquor treated cold with barium carbonate. The ferric oxide alone is precipitated; the barium carbonate, with which it was mixed, is readily separated. The liquor containing the nickel is treated with sulphuric acid, and after filtration is added to the ammoniacal solution of the rest of the nickel: this is precipitated by excess of potash, and after drying and calcining, is weighed; its quantity indicates that of the metallic nickel. The ammoniacal liquor, afterwards treated with ammonium sulphide, sometimes yields a black precipitate, which, collected, calcined, and weighed, gives with borax the reaction of cobalt.

Nickel is separated from manganese and zinc by the annexed process of EBELMEN. Put the weighed mixture of the oxides in a small platinum vessel, insert this into a tube, heat the mixture to dull redness, conducting all the time sulphuretted hydrogen gas over it. Let the sulphides formed cool in the gaseous stream, and then digest them for several hours with cold dilute hydrochloric acid, which dissolves only the sulphides of manganese and zinc. The sulphides of cobalt and nickel are left behind in a perfectly pure state, and may be separated, if desired, as above, by dissolving in aqua regia, &c.

R. FRESENIUS points out that, in analyzing nickel ores, it is essential to guard against imperfect separation from alumina, iron, and magnesia, &c., which sometimes greatly increase the apparent amount of nickel present.

His method of working contains no new process of separation. The ore is dissolved in aqua regia, precipitated with sulphuretted hydrogen, the precipitate filtered off, and the filtrate oxidised with nitric acid, excess of ammonia being then added to throw down the iron. Care must be taken to see that the iron precipitate contains no nickel. The filtrate is acidified with acetic acid, and after addition of sodium acetate treated with sulphuretted hydrogen, by which means the nickel and cobalt are obtained as sulphides. These sulphides are dissolved and precipitated with caustic potash, the oxides obtained are reduced in a stream of hydrogen, and the metals weighed. The metals are redissolved, and the solution treated with ammonia and ammonium carbonate, by which means generally a little precipitate of iron and alumina is obtained, while the silicic acid is left undissolved. This process is repeated with the precipitate, and the necessary subtraction made from the weight of the metals previously obtained.

If the ores contain zinc, it will be precipitated with the nickel and cobalt. In this case the solution of the sulphides is evaporated to a small bulk, and pure, finely crystallized sal-ammoniac added (about 5 grams. of sal-ammoniac to 0·2 gram. of zinc oxide); the mass is then dried on the water-bath and carefully treated, till all the sal-ammoniac, and with it the zinc, is removed.

When nickel or cobalt chloride is heated with sal-ammoniac not the slightest loss is occasioned, while zinc is totally expelled.

To separate nickel from cobalt:—If the nickel is in excess, the cobalt is removed as nitrite of potassium and cobalt; if the cobalt is in excess, the solution of the chlorides is treated with potassium cyanide in excess, pure caustic potash added, and the nickel precipitated by bromine.

For the analysis of nickel-glance R. FRESENIUS advocates the following method:—

An accurately-weighed sample of the ore is fused with eight times its amount of a mixture of equal parts of sulphur and sodium carbonate; the fused mass is treated with hot water; and the finely crystalline residue of metallic sulphides is filtered off and well washed, by which operation arsenic and antimony pass into solution.

After igniting the filter the residue is treated with fuming nitric acid, and evaporated to dryness. The small amount of lead sulphate remaining undissolved is not filtered off, but sulphuretted hydrogen is passed through the acid liquor until the latter is completely saturated with it. The filtrate from the sulphides of copper and lead is evaporated to dry-

ness: the ferrous oxide is oxidised with potassium chlorate; a little hydrochloric acid is added; and the solution is then largely diluted, and carbonate of soda added till the reaction is nearly neutral; then acetic acid is poured in drop by drop, till a clear brown solution of acetate of iron and nickel is formed. This done, the solution is heated to boiling, and when it is in that state the basic salt of iron must at once be filtered off and washed. After this precipitate is redissolved, and again precipitated in the basic state as before, a little of the precipitate must be tested to ascertain whether it is free from nickel; if not, the above operation must be repeated till all the nickel is removed. The filtrates from the precipitate must be brought together and evaporated to a moderately small bulk. The solution is heated to boiling, and caustic potash is then added in slight excess. The hydrated nickel oxide is washed and ignited, and then reduced in a stream of hydrogen gas. The resulting metal is now brought on a small filter, and treated with boiling water to remove any traces of caustic potash; after ignition of the filter it is again heated in a stream of hydrogen and weighed. The small amount of silica it contains is separated by dissolving the metal, evaporating the silica to dryness, and estimating the amount which is to be subtracted from the total quantity.

Electro-Deposition. — Nickel is largely used in electro-plating (see Electro-Metallurgy). The following process is said to work well:—1250 grams. of citric acid, 500 grams. of ammonium chloride or sulphate, and 500 grams. of ammonium nitrate are dissolved in 15 litres of water; the solution heated to 80° C., and freshly-precipitated nickel hydrate added to saturation. The solution is then removed from the heat, 2·5 litres of ammonia solution added, and the whole diluted to 25 litres; 500 grams. of ammonium carbonate are dissolved in the liquid, which is then filtered. On passing an electric current through this solution, nickel is separated as a white metallic deposit. During the deposition the temperature must not be allowed to sink below 50° C. It is essential that the nickel sulphate be tolerably pure.

The nickel of commerce is seldom pure, the percentage of metal often falling as low as 56 per cent., and seldom exceeding 88 per cent.

A. Terreil prepares pure nickel sulphate from commercial nickel containing 40 to 90 per cent. of the metal—the impurities being copper, iron, and small quantities of arsenic—by the following method:—The alloy is dissolved in aqua regia, and the solution evaporated almost to dryness. On treatment of the residue with water, some iron arsenate remains undissolved, and is separated by filtration. The copper is precipitated from the solution by introducing some iron tacks, and the iron in the solution is peroxidised; then a quantity of sulphuric acid is added sufficient to convert all the iron and nickel present into sulphates; the solution is evaporated to dryness, and the residue is treated with water, yielding a solution from which the iron is precipitated by barium carbonate. The filtrate, on evaporation, deposits crystals of pure nickel sulphate.

J. M. Merrick adopts a very ready method of determining the amount of nickel available for electrotyping in a given solution.

A platinum crucible, holding the solution to be decomposed, is made the negative pole of a two or three-cell Grove's battery, by placing it in the coiled-up end of the wire from the zinc plate, and the circuit is completed by dipping into the solution, through a perforated porcelain cover, a platinum wire from the other pole. The results obtained very accurately represent the percentage of nickel in solution, if no other metal is present capable of being precipitated by the current.

Alloys of Nickel.—Faraday states that meteoric iron can be imitated by fusing iron with nickel. The alloy of 90 iron with 10 nickel is of a whitish-yellow cast, and not so malleable as pure iron. The alloy with 3 per cent. of nickel is perfectly malleable and whiter than iron. These alloys are less disposed to rust than pure iron, but nickel alloyed with steel increases the tendency to rust.

With *copper* nickel forms a hard white alloy. The *white copper* of the Chinese, or *pakfong*, consists, according to the analysis of Dr. Fyfe, of 40·4 parts of copper, 31·6 of nickel, 25·4 of zinc, and 2·6 of iron.

German Silver (See Copper Alloys).—A similar alloy is largely used as a substitute for silver or for plated articles, under the name of *German silver*. It should consist of 1 part of nickel, 1 of zinc, and 2 of copper; or, when intended for rolling, of 25 parts of nickel, 20 of zinc, and 60 of copper; to which, if for *casting*, 3 of lead may be added. The following details respecting the alloys of nickel are by Messrs. Topping. The metals referred to should be as pure as possible.

Common German Silver.—Copper 8, nickel 2, zinc 3·5. This is the commonest that can be made with regard to the quality of the article produced, and may be used for ware for ordinary purposes. If the quantity of the nickel be reduced much below this the alloy will be little better than pale brass, and tarnish rapidly.

Good German Silver.—Copper 8, nickel 3, zinc 3·5. This is a very beautiful compound. It has the appearance of silver a little below standard; by some persons it is even preferred to the more expensive compounds.

Electrum.—Copper 8, nickel 4, zinc 3·5. This compound is superior to any of the others. It has a shade of blue like very highly polished silver; it tarnishes less easily than silver.—Copper 8, nickel 6, zinc 3·5. This is the richest in nickel that can be made, without injuring the mechanical properties of the metal. It is a very beautiful compound; but requires a higher heat for fusion than the preceding, and will be found rather more difficult to work.

Tutenag.—Copper 8, nickel 3, zinc 6·5. The proportions were originally obtained by analyzing a piece of Chinese tutenag of the best ordinary quality; but some rare specimens of Chinese tutenag, equal to electrum, have been seen. This alloy is very

fusible; but very hard, and not easily rolled. It is best adapted for casting.

German silver containing 15 per cent. of nickel is remarkable for its malleability, homogeneity, and whiteness. It may be drawn into wires, or rolled into sheets of any thickness, and is well adapted for ornamental work of every description.

Oxides.—Nickel forms two oxides: a monoxide, NiO, and a sesquioxide, Ni_2O_3.

Monoxide of Nickel may be procured in the anhydrous form by igniting the carbonate in a covered crucible, when it is left of an olive-green colour. It may be precipitated from its salts by potassium as a bulky light green hydrate (NiHO), and may be obtained crystallized by boiling carbonate of nickel in ammonia. Oxide of nickel forms insoluble compounds with potash or soda, which, however, may be decomposed by frequent washing with boiling water. Ammonia dissolves it, forming a deep blue solution. When fused with borax the oxide tinges the glass of a hyacinth yellow, which becomes less intense on cooling.

Sesquioxide, Ni_2O_3, is a black powder, which may be procured by passing chlorine through hydrated monoxide suspended in water, or by treating a nickel salt with bleaching powder. It is singular that it does not combine with acids, but gives off a portion of its oxygen by ignition, or by heating with nitric or sulphuric acids, which form with it salts of the *protoxide*.

Sulphide of Nickel, NiS, occurs native in greyish or yellowish capillary crystals; it may be produced artificially by fusion, and can be obtained as a black hydrate, when a salt of nickel is precipitated by sulphide of ammonium.

Chloride of Nickel, $NiCl_2$, is formed by dissolving the oxide in hydrochloric acid.

Sulphate of Nickel, $NiSO_4 + 7H_2O$, which results from the action of sulphuric acid on the metal, or its oxide, crystallizes in green rhombic prisms; these, when exposed to light, are converted, without loss of water, into small regular octohedra, aggregated together in the form of the original crystal, which becomes opaque.

The salts of this metal are of a delicate green hue, both when in the solid state and in solution. They have a sweetish astringent metallic taste.

Before the blowpipe salts of nickel give, in the oxidating flame, with biborate of soda, a reddish-yellow glass, which becomes much paler as it cools. In the reducing flame, greyish particles of reduced nickel are disseminated through the bead.

In solution *sulphide of hydrogen* gives no precipitate if the liquid be acidulated with sulphuric acid. *Sulphide of ammonium* gives a black sulphide. *Ammonia* gives a pale green deposit, soluble in excess of ammonia, forming a bright blue solution. *Potash* and *soda* throw down a pale green bulky hydrated oxide of nickel. The *carbonates of the alkalies* give a pale apple-green precipitate of basic carbonate of nickel, which is readily soluble in carbonate of ammonia. *Ferrocyanide of potassium* affords a greenish-white, and *ferridcyanide of potassium* a yellowish-green precipitate.

In analysis monoxide of nickel is always weighed as such. Mix the acid solution of the oxide in a beaker glass with pure potash or soda in excess, heat for some time to near boiling, filter, wash the precipitate thoroughly with hot water, dry, and ignite. The presence of ammoniacal salts, or of free ammonia, does not interfere with the precipitation. This method, if carefully executed, gives exceedingly accurate results, which the editor has often confirmed.

The nickel obtained in this country is chiefly employed for the manufacture of Argentane or German silver, which, as stated above, is an alloy of this metal with zinc and copper. Nickel likewise forms one of the constituents of the tutenag of China, and the pakfong of the East Indies. Being exclusively used as an alloy, the nickel of commerce comes into the market in the form of finely-divided grains, or granulations, of the size of small beans.

NITRIC ACID. — *Nitric Monohydrate*, *Hydrogen Nitrate; Acid Nitrique*, French; *Salpetersäure*, German. Symbol, HNO_3.—Nitric acid is a monohydrate of nitrogen pentoxide; it is constituted of—

Nitric anhydride or anhydrous nitric acid,	1 eq. = 108	N_2O_5
Water,	1 eq. = 18	H_2O
	126	$H_2N_2O_6 = 2HNO_3$.

It is a colourless transparent liquid, specific gravity 1·52; boiling at 86°, and leaving a weaker acid, which is held to be a sesquihydrate, $2HNO_3 + 3H_2O$, and has the specific gravity 1·42.

Liquid nitric acid was known as far back as the seventh century by Geber, who called it "solutive water." It has sometimes been called azotic acid, and in the time of the alchemists it was known as aquafortis—a name still retained. This acid was distilled from saltpetre as long ago as the thirteenth century by igniting the saltpetre with clay, or with copperas, in a retort. In fact, it is now well known that before the manufacture of sulphuric acid on an extensive scale, copperas played a most important part in the separation of nitric acid and muriatic acid from their alkaline bases.

The nature of its constituents was shown by Cavendish in 1785, and their more exact proportions were subsequently determined by Davy, Gay-Lussac, and Thompson. Cavendish made the accidental discovery in the course of his experiments on the formation of water by the combustion of hydrogen in the presence of common air, and he detected nitric acid in the water so formed. Still more recently these experiments have been verified by Faraday, who has gone into many interesting experiments in reference to the presence of nitrate of ammonia in the rain water of thunderstorms. In warm climates, especially where there is an abundance of decaying organic matters, and where its rapid decomposition spreads a supply of ammonia into the atmosphere, the formation, first of nitric acid, and then of nitrate of ammonia, proceeds most actively. On the Continent, both in France and Germany, artificial nitre beds are sometimes formed, from which considerable quantities of nitrates are ob-

tained. From the floors and outhouses of old stables and cow byres nitrates were obtained in 1789, during the French Revolution, when all other supplies were cut off from France by the allied armies. The short supply of this article at that time led to urgent appeals from the then government to encourage the adoption of new methods for producing nitrate of potash for the manufacture of gunpowder; and these appeals led to the establishment of chemical works near Paris by LE BLANC and others for the manufacture of carbonate of soda. Nitrate of lime is sometimes formed in warm weather in this country in the lime of old walls, from which the efflorescence can be collected.

In the *Philosophical Magazine* (1827) GRAHAM gives an account of LONGCHAMP'S theory on nitrification, read before the Academy of Sciences, in which he has developed a theory of the natural production of nitre in various soils, and superficially upon certain rocks.

Persons employed in the production of nitre know well that earths taken from caves furnish nitrates by lixiviation; and that earths replaced in the same places yield again, after eight or ten years, new quantities of saltpetre; and the nitrifaction is perpetual, without limit, provided that the returned earth possesses a sufficient portion of the base, which commonly solicits the formation of the nitric acid, and absorbs that acid as it is produced.

LAVOISIER took from a quarry a number of specimens of chalk at Roche Guyon and Mousseaux; and all, when washed, gave a small quantity of nitrate of potash, mixed with much nitrate of lime. These specimens were taken at a spot many miles away from any human habitation; and he draws the conclusion that nitric acid does not pre-exist in the chalk of Roche Guyon, but is formed by the action of the air. THOUVENEL also concludes that it is demonstrated by his experiments that atmospheric air possesses all that is necessary to serve for nitrification, as well as the air which emanates from putrescent bodies, provided that it finds matter capable of absorbing the materials.

It is universally admitted that nitric acid is not formed in sheltered places, unless a certain degree of humidity prevails, and the air circulates through all the parts, for in places where the air cannot be renewed there is no formation of acid; and it is necessary that the rock or earth should be porous, such as light soils, tufa, chalk, and porous limestones. Marble or hard mountain limestone have no property in the formation of nitrates. These porous substances contain moisture, and the water contains oxygen and nitrogen, and also free carbonic acid. This free carbonic acid renders a portion of the carbonate of lime soluble in the water or moisture, which must be present, and thereby enables the carbonate of lime to act more effectually upon the oxygen and nitrogen which the water has absorbed. The oxygen, nitrogen, and carbonate of lime are all liquid, and in solution in the water; they are therefore in circumstances most favourable to their mutual action.

Dr. PALMER, on the "North-western Provinces of India" (*Chemical Society's Journal*, 1868), gives an account of the formation of nitrate of potash in the plains of India, from whence the chief supply is obtained. He says its production is most abundant in the parts most distant from the mountain ranges. The soil in these parts is composed of a very uniform alluvium, or river sand, for a depth of more than 200 feet, the uniformity of this is only broken by occasional layers of clay; but where the depth of soil is shallow, and water is within a few feet of the surface, no nitrate is formed. For eight months of the year no rain falls in these nitro-producing parts of India; the soil is exposed to the continuous influence of dry wind and a burning sun. The villages situated in these districts are large and very thickly populated, and the houses are mostly built of mud walls, and each family has at least a pair of plough oxen. The only drains from the houses and the cow byres are small surface drains, and the only fluids which pass by these drains are urine and the small quantity of refuse water used in cooking. The drains usually open on a small open plot of ground, where the drainage diffuses itself, and is rapidly dried in the sun. The wood ashes used for the cooking fires are also thrown out on this same plot of ground, and we have then all the elements which, after decomposition, are necessary for producing nitrate of potash. As soon as it is seen that a white efflorescence appears, a thin layer is scraped from the ground, and is removed for lixiviation and crystallization. A continuous production of nitrates is thus going on in these villages from generation to generation, and from this production the wants of Europe are supplied.

An interesting paper has been published, by THORNTON J. HERAPATH, to show that this acid was known to the ancient Egyptians. In his *brochure* HERAPATH gave a short account of some experiments he had made on certain hieroglyphical marks or letters that had been discovered on the wrappers of a mummy which was unrolled by NASH at the Bristol Microscopical Society; and as the result of these he stated his belief that the ancient Egyptians were acquainted with a marking fluid containing nitrate of silver for its basis, and were also familiar with the use of nitric acid. A short time afterwards, DENHAM SMITH, in replying to this paper, took exception to these views; and whilst admitting the interesting nature of the discovery that had been made of an argentine solution having been employed some three thousand years ago, as *marking ink*, totally dissented from the conclusions that had been founded on it, inasmuch, he said, as there was no evidence to prove that the Egyptians were even versed in the art of distillation. He also hazarded the opinion, unsupported, however, by direct evidence, that the marking fluid in question was prepared by dissolving either the chloride or oxide of silver in an ammoniacal solution, and consequently without the intervention of any acid whatever. As the question in dispute is one of great interest in a scientific point of view, HERAPATH

pursued the subject, and submitted the marks to a fresh examination. After making several preliminary experiments, he found that no results of any value could be obtained by the ordinary modes of analysis, and was therefore compelled, as a last resource, to call in the aid of the microscope.

On examining with this instrument some of the fibres of the bandages that were stained by the argentine ink, he found them to present a very singular appearance. The ends near the corroded parts of the fabric were stained of a deep brown or black; but for some little distance beyond the blackened portion the fabric had a pale yellow hue, as if, during the decomposition of the silver salt that had been employed as *marking ink*, the nitrogenous constituents of the tissue had been partially acted upon, and converted into xanthoproteic acid.

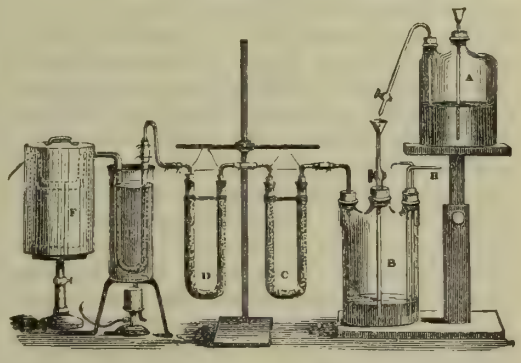
Between several of the fibres, and in many places adhering to their external surfaces, were found small particles of some organic tissue, which were tinged of a still deeper yellow than the fibres themselves. On subjecting some of the latter to the action of strong liquor ammonia, the yellow portions, particularly the altered intercellular substance, acquired a still darker hue, whilst those, on the contrary, which were stained by the reduced silver became slightly paler, as if a part of the argentine film was soluble in that liquid; though it should be observed that no further effect was produced on the stain, even by a lengthened digestion in ammonia. Now, upon making comparative experiments with a piece of the linen wrapper that had been previously marked in the ordinary manner with solution of nitrate of silver, the fibres were found to present an appearance very similar to that above described, the only difference being that the yellow coloration was not quite so palpable, and more of the silver stain was eradicated by the solution of ammonia; whereas, on the other hand, fibres that had been stained by solutions of chloride and oxide of silver in ammonia, were uniformly coloured of a dark brown or black, and exhibited no remnant of the yellow coloration.

On the whole, the results of Herapath's microscopic examination appear to justify the conclusion that the ancient Egyptians were really familiar with nitric acid and its uses, and actually employed the nitrate of silver as a marking fluid. In what way, however, they prepared the acid—whether by distillation of the sodium nitrate or of potassium nitrate with sulphuric acid—may for ever remain a mystery.

Nitric acid can also be formed when nitrogen-dioxide (formerly termed nitric oxide) is mixed with oxygen over water: 4 volumes of nitric oxide condense 3 volumes of oxygen; but nitric oxide and oxygen never combine in these proportions without the presence of water or a solution of an alkali.

Deville has tried several interesting experiments in attempting to make anhydrous nitric acid, and the following is the description given by Miller, who says that nitric acid may be obtained anhydrous by Deville's method, in which state it forms perfectly transparent, brilliant, colourless crystals, derived from the right rhombic prism; they melt at 30°, and boil at 45° to 50° C.; at about this temperature the compound begins to be metamorphosed. Sometimes the crystals, even if kept in sealed tubes, undergo decomposition at the ordinary temperature, and the tube bursts with a dangerous explosion, from the pressure exerted by the liberated gases. The crystals dissolve rapidly in water, emitting much heat, and producing ordinary nitric acid. The process consists in passing a uniform current of perfectly dry chlorine gas very slowly over crystals of well-dried nitrate of silver; the salt is heated to about 93° C. at first, till the decomposition has commenced, and the temperature is then lowered to about 65° C. The operation is one of considerable delicacy, and requires attention to a number of minute precautions. The apparatus required is shown in Fig. 1. A is a vessel of concentrated sulphuric acid; the acid is drawn off from it by the siphon, and allowed to flow into the vessel, B, in a very slender stream, which can be regulated by the glass stopcock; B has also been filled with sulphuric acid, and subsequently charged with pure dry chlorine, by means of the bent tube, H. C is a tube filled with dry chloride of calcium;

Fig. 1.



D, a tube filled with pumice, moistened with sulphuric acid; E, a tube filled with nitrate of silver in crystals, immersed in a bath of oil; F, the receiver for the anhydrous nitric acid, which is kept cool by a mixture of ice and salt. The tubes E and F are made of one continuous piece of glass, as the acid immediately attacks and destroys cork or caoutchouc joints; a portion of one of the lower oxides of nitrogen is liquefied and collected in the tube in F, and is then separated. The chlorine displaces the nitric acid and oxygen from the nitrate of silver; chloride of silver is formed, and the nitric acid and oxygen escape. By surrounding the receiver, F, with a freezing mixture, the nitric acid is condensed in crystals. The decomposition is of the following simple character:—

Nitrate of silver.	Chlorine.	Chloride of silver.	Oxygen.	Nitric anhydride.
Ag_2O,N_2O_5	+ $2Cl$	give $AgCl$	+ O	+ N_2O_5

The composition of anhydrous nitric acid was determined by Deville, by estimating the quantity of nitrogen which a given weight of the acid furnished after the oxygen had been removed from it by heating it in contact with copper, which rapidly

combines with oxygen at a higher temperature. DEVILLE found in one of his experiments, that 547 milligrammes of acid gave 116 cubic centimètres of nitrogen at a temperature of 5° C. whilst moist, and under a barometric pressure of 757 millimètres. This, when corrected, gives in 100 parts of the acid by weight 25·9 of nitrogen; the deficiency, 74·1, is oxygen, or 14 parts of nitrogen are united with 40 of oxygen.

According to Dr. URE, who examined the properties of nitric acid very fully about the year 1818, we find that nitric acid of specific gravity 1·50 boils at 210° Fahr., at 1·45 it boils at 240° Fahr., at 1·42 it boils at 253° Fahr., and at 1·40 it boils at 246° Fahr. If an acid stronger than specific gravity 1·420 is distilled in a retort, it gradually becomes weaker; and if weaker than 1·42 it gradually becomes stronger till it assumes that standard of density. Acid of specific gravity 1·485 has no more action upon tin than water has, though when it is either stronger or weaker it oxidises it rapidly, and evolves fumes of nitrous acid gas with explosive violence. In two papers upon nitric acid, published by Dr. URE in the *Journal of Science*, 1818 and 1819, he investigated the chemical relations of these phenomena: acid specific gravity 1·42 consists of 1 atom of dry acid and 4 atoms of water; acid of 1·485, of 1 atom of dry acid and 2 atoms of water; the latter compound possesses a stable equilibrium as to chemical agency, the former as to calorific. Nitric acid of specific gravity 1·334, consisting of 7 atoms of water and 1 atom of dry acid, resists decomposition by light. Nitric acid acts with great energy upon most combustible substances, giving off oxygen to them, and resolving itself into nitrous gas, or even nitrogen. Such, for instance, is its action upon hydrogen, phosphorus, sulphur, charcoal, sugar, gum, starch, silver, mercury, copper, iron, tin and other metals. When nitric acid is mixed with snow, the latter is liquefied, and intense cold is produced. Nitric acid of specific gravity 1·50 mixed with half its bulk of water occasions an elevation of temperature in the mixture equal to 112° Fahr., and 58 parts of acid with 42 parts of water, both at 60° Fahr., give when mixed a temperature of 140° Fahr. (URE, *Quart. J. of Science*). On diluting the red fuming acid, or the strong nitro-sulphuric acid produced from a GAY-LUSSAC tower, it assumes various tints of bluish green, depending upon the quantity of water added.

Dr. TURNER says, that when nitric dioxide is passed through concentrated nitric acid it is decomposed, and nitrous acid is formed, partly by the acquisition of oxygen by the oxide, and partly by its loss by the acid. The nitrous acid thus derived from two sources gives a colour to the nitric acid, the depth and kind of which depends upon the quantity of the deutoxide of nitrogen which has been employed. The first portion communicates a pale straw colour, which gradually deepens as the absorption by the deutoxide continues, till the nitric acid has acquired a deep orange colour, together with all the characteristics of fuming nitrous acid. By applying heat to the blue liquid, the dioxide of nitrogen is evolved, and in proportion as it escapes the colour of the solution changes to green, olive, orange, and yellow; at length becoming pale as at first.

Nitrous acid vapours are likewise disengaged as well as dioxide. These phenomena are very favourable to the view that the conversion of the orange colour into olive-green and blue is owing to the formation of hyponitrous acid. Some of the metals, such as copper, tin, and silver, are at first without action on concentrated nitric acid, but become violently active upon the addition of a little water. Poured upon hot iron filings, or melted bismuth, zinc, or tin, nitric acid causes a combustion of the metals. In its action upon metals which decompose water, nitric acid gives rise to the formation of ammonia and nitrate of ammonia, a fact long known to PAYER and other French chemists. The facility with which nitric acid imparts oxygen renders it a valuable oxidising agent. Phosphorus decomposes it at common temperatures, and sulphur and carbon when aided by heat. A piece of glowing charcoal thrown upon the surface of concentrated acid burns with evolution of red fumes (BERZELIUS). It acts on a large number of organic bodies, and mutual decomposition ensues. A drachm of oil of turpentine mixed with half a drachm of sulphuric acid instantly bursts into flames upon the addition of a drachm of nitric acid. Malic, oxalic, and carbonic acids are the common products of the action of dilute nitric acid upon many vegetable substances; ammonia and hydrocyanic acid are also sometimes formed. It tinges many animal substances a yellow colour, and permanently stains the fingers and nails, as most young chemists soon find out.

It is used for etching on copper, and as a solvent for tin in the preparation of valuable mordants used by dyers and calico printers. In medicine it is prescribed as a tonic, and occasionally in hepatic and eruptive diseases, and in surgery as an energetic caustic.

Exposure to the light of the sun produces its partial decomposition, and, as has already been remarked, mere distillation of the compound has invariably the same effect.

Nitric acid is an important agent in analysis. It is used—1. To oxidise and dissolve the metals, and to separate them from the few which are not acted upon by it, especially gold and platinum, and it is in constant use in assaying for separation of silver and gold. 2. To separate certain metals in the form of insoluble peroxides—such as antimony and tin—from those which yield soluble oxides, as in the separation of tin from mercury. It is also useful in the peroxidising of iron and manganese, by which those metals are rendered insoluble in nitric acid, and thus easily separated from soluble earths, &c. 3. Dilute nitric acid separates sulphur from the metals and some of the earths in the form of an insoluble magma, as in the analysis of sulphuret of copper, of lead, or of silver; but if concentrated, it acidifies sulphur and arsenic. 4. The concentrated acid detects sulphuretted hydrogen by the production of a white cloud, and the destruction of its

fetid odour. 5. It is used as a solvent to determine the nature of certain precipitates, and to separate the soluble from the insoluble. 6. Nitric acid is a test for certain organic substances, and it generally tinges those containing nitrogen a yellow colour; it detects strychnia by rendering it a red colour; it distinguishes gum from starch by converting the former into mucus, and cork is converted into suberic acid. 7. Nitric acid, as well as many of the nitrates and nitro-hydrochloric acid, are used as valuable chemical reagents.

Tests for Nitric Acid.—No ready method is known of precipitating nitric acid from its solutions, since all its compounds dissolve more or less freely in water. Various indirect methods have been recommended for discovering its presence. One of the best consists in neutralizing the solution, if acid, with potassium hydrate, and evaporating nearly to dryness; then adding a few copper filings, and heating the mixture with a little sulphuric acid. The copper combines with a portion of the oxygen of the nitric acid, and decomposes it, while characteristic red fumes due to nitrogen dioxide show themselves if nitric acid be present. A still smaller quantity of the acid may be detected by substituting a crystal of ferrous oxide for the copper, before adding the sulphuric acid; on the application of a gentle heat in this case, the characteristic action consists in the formation of an olive-green solution, the colour of which disappears on boiling. The nitrous acid gas, formed by the deoxidising action of one portion of the iron salt, dissolves, with the distinctive green colour, in the solution of the unoxidised part of the salt. If a few drops of hydrochloric acid be added to a solution which contains free nitric acid, or a nitrate dissolved, the liquid acquires the power of dissolving gold leaf. This effect, however, is produced by hydrochloric acid in solutions of the iodates, chlorates, and bromates, but the presence of these salts may be detected by other characters. Price's test for the detection of iodine is equally applicable for the detection of nitric acid.

Liebig has suggested the following tests:—The liquid to be examined must be mixed with a sufficiency of sulphuric solution of indigo to acquire a distinct blue colour. A few drops of concentrated sulphuric acid are then added, and the whole boiled; if the liquid contains a nitrate, it will either be bleached or rendered yellow. By adding a little common salt to the liquid before applying heat a $\frac{1}{5000}$th part of nitric acid may be discovered. M. Runge has suggested to detect nitric acid and its combinations as follows:—Pour a solution of protochloride of iron upon the surface of an amalgam of zinc, and then place a crystal of nitre on the latter in the fluid; a dark band immediately forms around the crystal, sometimes extending over the whole surface of the amalgam. All the nitrates, as well as nitric acid, act in this manner; but other salts, such, for instance, as the chlorates, produce no such effect, so that a sensible test of the presence of nitric acid is given. It is necessary that the solution employed be a protosalt of iron. If nitric acid is supposed to be in the liquid, it should be saturated with potassa, evaporated to dryness, and the dry mass tried. Salts of copper and silver must not be present (Graham, 1827).

Kane says that the detection of nitric acid is not difficult; it cannot be recognized by forming precipitates, as all its neutral salts are soluble, but its properties are very marked. 1. The production of red fumes of nitric dioxide when it is brought into contact with a metal is characteristic of it. 2. When a drop of nitric acid is added to water tinged blue by sulphate of indigo, and the mixture boiled, it is bleached by the oxidisation of the indigo by the acid. 3. When a small crystal of protosulphate of iron is placed in contact with water containing nitric acid, a ring of deep olive coloured liquid forms round it, according as it dissolves. 4. Nitric acid confers upon muriatic acid the power of dissolving gold leaf; but this test is not of such distinctness as the others. 5. Nitric acid may also be distinguished by the deep red colour it produces with a crystal of morphia (Kane).

The usual impurities in nitric acid are hydrochloric acid (arising from the nitrate of soda, from which it is manufactured, containing common salt and sulphuric acid, owing to the manufacture having been carried on at too great a heat), and iron obtained from the metal cylinders used in the decomposition. These impurities are easily detected; the first with nitrate of silver, which causes a white precipitate of chloride of silver; the second, by chloride of barium, which gives a precipitate of sulphate of baryta; and the last, by prussiate of potash, which gives a blue precipitate of prussiate of iron (R. C. Clapham).

In the laboratories of the extensive chemical works on the Tyne and in Lancashire, different methods of treating the nitrous and nitric acid in the "nitrous vitriol" run from the Gay-Lussac absorbing columns have been carried out for many years. It is necessary that the test in daily use should not only be practically accurate, but also sufficiently rapid in its action, so as not to delay the chemist in his work. The old plan adopted by foremen of works for many years, and which to some extent gave practical results, was to rapidly pour equal measures of water and nitrous vitriol together, and then judge of the extent of the saturation of nitrous acid by the red fumes given off. The more accurate methods, however, in daily use, are the application of the tests of bichromate of potash, permanganate of potash, nitrate of urea, and bleaching powder. Standard solutions of these salts are prepared and kept ready for use, and in all cases it is found best to pour the nitrous vitriol into the measured quantity of the test liquor, rather than pour the test liquor into the acid.

Of these tests the permanganate and bichromate give the most reliable results. The nitrate of urea is very variable and unsatisfactory; and the bleaching powder test, although still adopted by some firms as sufficiently practical for their wants, is not always reliable in its results.

Very recently a paper on this subject was read before the members of the Newcastle-on-Tyne

Chemical Society by Dr. Lunge of Zurich, which describes very fully the best methods of testing nitric and nitrous acids, and from which we give the following extracts (R. C. Clapham):—

Estimation of Nitric Acid.—One of the oldest, and probably the most widely-used method of estimating nitric acid, is that first proposed by Pelouze, but considerably modified by Fresenius, viz., dissolving metallic iron in hydrochloric acid, and adding the compound containing nitric acid, or one of its salts, heating till the action of NO_3H on the ferrous salt is complete, and all NO is given off; and estimating the unoxidised portion in the ferrous salt by means of potassium bichromate or permanganate. In the latter case sulphuric acid must be employed for dissolving the iron. If the air has access to the liquids during these operations, there may be some oxidation of ferrous to ferric sulphate at the expense of atmospheric oxygen; but a more serious source of error is the regeneration of nitrogen acids from the evolved NO, which act again upon ferrous sulphate, and thus too high a proportion of nitric acid is indicated by the process. The process, as originally proposed by Pelouze, is certainly altogether faulty; but it became most accurate when Fresenius proposed to conduct the operation with a number of precautions, the most important of which is the carrying on of the whole process in an atmosphere of carbon dioxide. The process of Fresenius is, however, somewhat lengthy and complicated, and entails the use of cumbrous apparatus, and this would militate against its use in many, especially in all works', laboratories. A modification is therefore adopted by very many chemists, consisting in dispensing with the current of CO_2; but conducting the operation of dissolving the metallic iron, and partly oxidising the solution by nitric acid or its salts in a flask fitted with a Bunsen's india-rubber valve; that is to say, a cork, through which passes a short glass tube open at both ends, but closed at the outer end by means of a small piece of india-rubber tubing, and a bit of glass rod stopping the latter again. The india-rubber tubing is provided with a sharp longitudinal incision of about 1 centimètre's length, which allows any gas or vapour to pass out, but none to enter into the tube, and thence into the flask. In this apparatus the steam arising from the boiling liquid soon expels the air, and prevents its injurious action upon the accuracy of the process; nor can the air enter again on cooling, as the valve prevents it from doing so, so that a vacuum is formed in the flask, which ought to be of strong glass to resist the atmospheric pressure. This apparatus is so very simple that even the smallest laboratory can use it; but doubts have arisen whether the results obtained by it are really trustworthy. I have therefore made with this apparatus a number of experiments (nine), in which I worked with every possible precaution against error, and in which I employed exactly known quantities of nitric acid or potassic nitrate. In order to save the time consumed by cleaning, accurately weighing, and dissolving the iron wire, I employed in this series of experiments, as well as in all those following, a solution of pure ferrous sulphate (100 grams. per litre), acidulated with 5 per cent. of sulphuric acid. Of this solution a certain volume, more than sufficient for the nitric acid contained in the test liquid, was employed, and a similar volume was tested at the same time by a standard solution of potassium permanganate; one such standardizing of the iron solution is sufficient for a whole day, as the free acid prevents its too rapid oxidation. The potassium permanganate solution itself was made from pure crystals, and standardized once a week with pianoforte wire in the same apparatus (taking 100 wire to contain 99·6 Fe); it was found to be unchanged after a month's standing.

The time consumed by each test till the NO was completely driven off was very inconveniently long, unless a large quantity of free acid was present, say 20 parts of SO_4H_2 to each 100 parts of liquid. If there is less acid present, the reaction, as shown by the colour of NO dissolved in the solution of the ferrous salt, goes on extremely slowly, or, with great dilution, not at all, until by prolonged boiling the above concentration has been reached. It is therefore convenient to add a sufficiently large quantity of pure strong sulphuric acid at once, in order to hasten the process. A pinch of sodium bicarbonate may be thrown in as well to fill the vessel with CO_2, but my results were as accurate without as with this modification.

With proper precautions, especially if the concentration and temperature of the liquids are not such as to cause an instantaneous reaction before the air has been expelled from the apparatus by aqueous vapour, the results obtained in all the nine experiments made by this process are as accurate as it can be expected by any method; and it can be recommended to chemists even in its simplified form, as described above.

The estimation of nitrous and nitric acid in the same sample can be effected in the most satisfactory way by first oxidising the nitrous acid by means of standard potassium permanganate, then adding a measured volume of a solution of ferrous sulphate of known relation to the permanganate, and finishing the process as prescribed for the estimation of nitric acid. From the total quantity of nitric acid thus found a deduction is made for that corresponding to the N_2O_3, the difference corresponding to the nitric acid originally present. It is only necessary to deduct one and a half times the number of c.c. first consumed for oxidising N_2O_3 into N_2O_5 from the number afterwards found (in the shape of ferrous sulphate) consumed for reducing N_2O_5 to N_2O_2; the remainder will show how much N_2O_5 (or rather NO_3H) was present. The whole operation is carried on from beginning to end in the same flask, fitted with a Bunsen's india-rubber valve, as above described. This I proved to be altogether correct by dissolving some pure potassium nitrate in my artificial nitrous acid prepared with silver. On testing, as by the plan just described, I found—1. Employed 0·2010 KNO_3, found 0·2012; 2. Employed 0·1950 KNO_3, found 0·1936.

A third blank experiment was made with the nitrous acid without adding any potassium nitrate. Originally used 10·2 c.c. permanganate; found to require for reduction, ferrous sulphate equal to 15·15 c.c. permanganate instead of 15·3; the 0·15 c.c. of permanganate used in excess of the theoretical quantity in re-titrating the iron solution would be required for staining the large volume of liquid obtained at the end, so that the blank experiment may be declared to be quite satisfactory.

It seemed to be desirable to apply the just-described process to the analysis of nitrous acid obtained on a large scale from the absorbing column of a sulphuric acid works. I procured such from a factory on the borders of the lake of Zurich. It had a specific gravity of 1·691, and was evidently almost saturated with N_2O_3. Eleven experiments proved it to contain 4·13 grams. N_2O_3 in 100 c.c. of acid (= 2·44 per cent. by weight). Now, the published analyses of nitrous vitriol generally mention the presence of NO_3H in the same as well. For instance, Winkler found 0·256 per cent., Kolb even 0·9 and 1·14 per cent., calculated as N_2O_5. It is not, on the face of it, clear how nitric acid can get into nitrous vitriol, since it cannot very well bodily traverse the chambers without being reduced to lower nitrogen oxides; and since it is not re-generated either from the latter in the presence of sulphuric acid, the oxidation in this case never going beyond N_2O_4, as proved by Winkler himself. Experiment has proved in my special case that the nitrous vitriol really contained no NO_3H whatever. The additional permanganate, over and above that corresponding to N_2O_3, amounted in two experiments to 0·05 and 0·1 c.c., which is just sufficient to stain the liquid; and I am inclined to believe that nitrous vitriol really does not contain any nitric acid, except perhaps traces, in any case; for I was able to show by experiment, performed purposely by the faulty method generally in use, that nitric acid was generated during the testing process where it did not exist before. My artificial nitrous acid, prepared from pure $AgNO_2$, and thus absolutely free from NO_3H, required, as mentioned above, for its reduction, after oxidation to NO_3H by means of permanganate, as nearly as possible exactly the theoretical quantity of ferrous sulphate—viz., that corresponding to one and a half times the quantity of permanganate first used. But this was only the case when the oxidation had taken place in the way described by me as the only accurate one—viz., by dropping the nitrous acid into the permanganate. When purposely the opposite way had been employed—viz., diluting the nitrous vitriol with very much water, then oxidising by permanganate, and reducing again—the following results were obtained:—1. Real percentage in 100 volumes of acid, 0·235 N_2O_3, 0·000 N_2O_5. Found by the above faulty method, 0·180 N_2O_3, 0·045 N_2O_5; the latter corresponding to 0·027 N_2O_3, leaves 0·028 for absolute loss (probably as NO). 2. Found 0·199 N_2O_3, 0·036 N_2O_5, the latter corresponding to 0·021 N_2O_3, leaving 0·015 for absolute loss.

It was thus positively proved that, by the more usual plan of testing nitrous vitriol, nitric acid is generated in the process of dilution, according to the equation—

$$3NOOH = 2NO + NO_2OH + H_2O.$$

—(Lunge.)

The following table, drawn up by Ure, and given in his "Dictionary of Arts," shows the specific gravity of the nitric acid—the liquid acid in 100 parts, and the dry acid in 100 parts:—

Specific Gravity.	Liquid Acid in 100 Parts.	Dry Acid in 100 Parts.	Specific Gravity.	Liquid Acid in 100 Parts.	Dry Acid in 100 Parts.	Specific Gravity.	Liquid Acid in 100 Parts.	Dry Acid in 100 Parts.	Specific Gravity.	Liquid Acid in 100 Parts.	Dry Acid in 100 Parts.
1·5000	100	79·700	1·4189	75	59·775	1·2947	50	39·850	1·1403	25	19·925
1·4980	99	78·903	1·4147	74	58·978	1·2827	49	39·053	1·1345	24	19·128
1·4960	98	78·106	1·4107	73	58·181	1·2826	48	38·256	1·1286	23	18·331
1·4940	97	77·309	1·4065	72	57·384	1·2765	47	37·459	1·1227	22	17·534
1·4910	96	76·512	1·4023	71	56·557	1·2705	46	36·662	1·1168	21	16·737
1·4880	95	75·715	1·3978	70	55·790	1·2644	45	35·865	1·1109	20	15·940
1·4850	94	74·918	1·3945	69	54·993	1·2583	44	35·068	1·1051	19	15·143
1·4820	93	74·121	1·3882	68	54·196	1·2523	43	34·271	1·0993	18	14·346
1·4790	92	73·324	1·3833	67	53·399	1·2462	42	33·474	1·0935	17	13·549
1·4760	91	72·527	1·3783	66	52·602	1·2402	41	32·677	1·0878	16	12·752
1·4730	90	71·730	1·3732	65	51·805	1·2341	40	31·880	1·0821	15	11·955
1·4700	89	70·933	1·3681	64	51·068	1·2277	39	31·083	1·0764	14	11·158
1·4670	88	70·136	1·3630	63	50·211	1·2212	38	30·286	1·0708	13	10·368
1·4640	87	69·339	1·3579	62	49·414	1·2148	37	29·489	1·0651	12	9·564
1·4600	86	68·542	1·3529	61	48·617	1·2084	36	28·692	1·0595	11	8·767
1·4570	85	67·745	1·3477	60	47·820	1·2019	35	27·895	1·0540	10	7·970
1·4530	84	66·948	1·3427	59	47·023	1·1958	34	27·098	1·0485	9	7·173
1·4500	83	66·155	1·3376	58	46·226	1·1895	33	26·301	1·0430	8	6·376
1·4460	82	65·354	1·3323	57	45·429	1·1833	32	25·504	1·0375	7	5·579
1·4424	81	64·557	1·3270	56	44·632	1·1770	31	24·707	1·0320	6	4·782
1·4385	80	63·760	1·3216	55	43·836	1·1709	30	23·910	1·0267	5	3·985
1·4346	79	62·963	1·3163	54	43·038	1·1648	29	23·113	1·0212	4	3·138
1·4306	78	62·166	1·3110	53	42·241	1·1587	28	22·316	1·0159	3	2·391
1·4269	77	61·369	1·3056	52	41·444	1·1515	27	21·517	1·0106	2	1·594
1·4228	76	60·572	1·3001	51	40·647	1·1467	26	20·722	1·0053	1	0·797

Nitric acid is now always manufactured from nitrate of soda, which is imported into this country from Peru and Bolivia, through the ports of Chili; and is used not only in the production of nitric acid

for sale, but still more extensively in alkali works and in manure works. The writer has obtained from R. HUNT, F.R.S., of the Jermyn Street Museum, the following information as to its importation into this country:—

	1874. Cwts.	1875. Cwts.	1876. Cwts.
Nitrate of soda imported,	2,117,170	3,382,636	3,298,277
Do. in value,	£1,270,673	£2,029,123	£1,890,827

In nearly all published works upon chemistry, the description given of the formation and natural deposits of nitrate of soda are very vague and misleading. It is therefore interesting to refer to Dr. FORBES' report on the "Geology of Bolivia and Southern Peru" (see *Journal of Geological Society*, 1860, and *Philosophical Magazine*, 1866), in which he gives a very clear and complete account of these important deposits. He concludes that nitrate of soda has been formed at the margin or fringe slopes of the ancient ocean tidal lagoons by the decomposition of sea salt, which was gradually deposited there on the upheaval of the coast, and which was effected by the agency of carbonate of lime and organic matters of all kinds—both terrestrial and marine vegetation, particularly the latter. These lagoons or swamps would be surrounded by a luxuriant growth of marine plants, of semi-aquatic habits; and although the country in the immediate vicinity is now a dry and arid plain, and without a drop of surface water, there are everywhere traces of the former vegetation discovered, in the enormous quantities of wood and trees of great size buried in the plains, as well as reeds, rushes, and other vegetable matter, and also sea-shells. He states that nitrate of soda does not represent any regular bed or deposit, but is only the out-crop of a bed of salt (with which all nitrate of soda is contaminated); or, in other words, it is the bed of salt left on the bottom and sides of the ancient lagoons after their complete desiccation, and at the edge of the sloping shore or bank, of which the salt has been more or less converted into nitrate of soda by chemical action. In the centre or lower parts of the salt bed nitrate is never found, but at the out-crop it is nearly always found in less or more quantity.—(FORBES.)

The following is an analysis of crude nitrate of soda from the ordinary virgin workings:—

Nitrate of soda,	21·01
Sulphate of soda,	4·74
Chloride of sodium,	55·27
Chloride of calcium,	0·33
Insoluble silica,	2·04
Sulphate of alumina,	9·81
Sulphate of magnesia,	5·93
Iodide of potassium,	0·87
	100·00

The quality of the nitrate of soda imported into this country, and which has been produced from the above crude native salt after lixiviation and crystallization, varies to some extent, its commercial value depending upon the amount of "refraction." The more impure cargoes are used for manure, whilst the others are employed in making nitric acid for sale, and in the extensive and important manufacture of sulphuric acid in chemical works. The following are analyses made by the writer from many hundred cargoes:—

Sulphate of soda,	0·81	0·46	0·25	1·40
Chloride of sodium,	1·21	0·50	0·32	0·76
Sulphate of lime,	0·71	0·12	0·52	0·12
Chloride of magnesium	0·80	—	0·31	0·12
Sand and insoluble,	0·92	0·40	0·42	1·00
Water,	1·10	0·60	1·20	3·50
Nitrate of soda,	94·45	97·92	96·98	93·10
	100·00	100·00	100·00	100·00

—(R. C. CLAPHAM.)

Nitric acid manufactured for sale on the large scale is produced in metal retorts set in brickwork, and heated from below by a fire. Fire-clay retorts, if practicable, would be better than iron; but are more difficult to heat equally, and are more liable to be broken by change of temperature. The retorts are usually 5 feet 6 inches to 6 feet 3 inches long, and from 20 to 24 inches diameter, with lids or doors at each end for charging and discharging the material. About 1½ cwt. to 2 cwts. of nitrate of soda are used as a charge, and strong sulphuric acid standing about 140° Twad. is run into the retort, care being taken that an excess of acid is always used, as a less produce of nitric acid is obtained if the charge of sulphuric acid is too small, owing to part of the nitric acid being liable to be decomposed by the heat into nitrous acid, part of which escapes, and the rest produces a red discoloration of the nitric acid.

Fig. 2 is a plan of the apparatus generally employed:—

A is the gauge acid cistern, with pipe leading to retort. B is the retort, containing a charge of nitrate, with moving doors at each end to receive and discharge the material, and for receiving a supply of sulphuric acid, and to allow escape of nitric acid. C is the fireplace. To produce a pure nitric acid a moderate heat should be applied to the retort, and a heat of about 260° Fahr. is sufficient for the purpose; but as this heat leaves a soft pasty mass of sulphate of soda in the retort, it is better to gradually carry the heat up to about 450° Fahr., which completes the operation, and produces a comparatively dry and commercial sulphate, called "nitre cake," which is disposed off to alkali makers, and brings a price varying from 35*s.* to 50*s.* per ton.

The nitric acid produced from the retorts is not all chemically pure. The chief impurities are hydrochloric acid and chlorides of iron, which come off at an early stage of the operation, and are condensed in the first condensing bottle, B, as shown in Fig. 3:—The middle bottles, C C C C, are found to contain the commercial nitric acid, and the last bottles, D D, which had been filled with water, contain the weak acid, and may in the next operation be substituted for the centre bottles, C, and is in this manner brought up to strength. A is the entrance-pipe from the retort, and E is the exit-pipe to chimney. As soon as the first half of the nitric acid has

passed off the temperature is allowed to rise, and the bisulphate reacts on the undecomposed nitrate, and the second half of the nitric acid is liberated.—(R. C. CLAPHAM.)

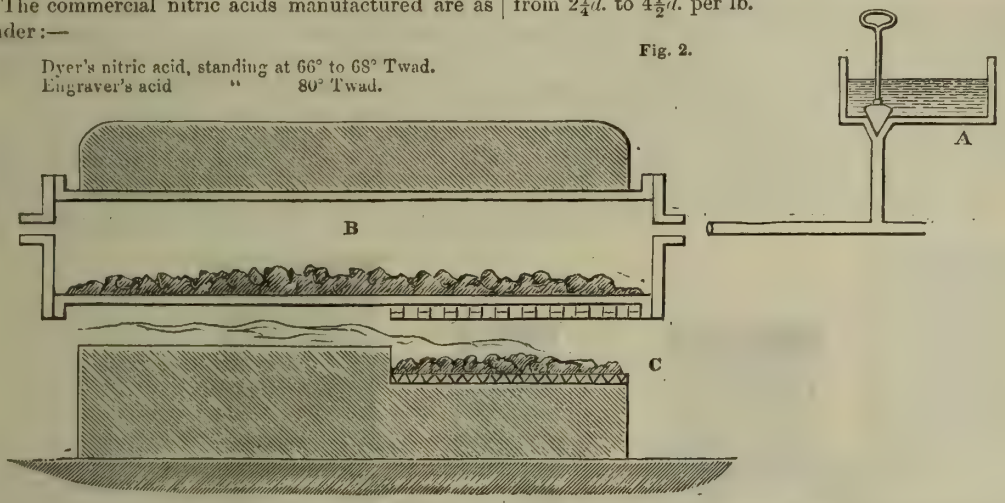
The commercial nitric acids manufactured are as under:—

Dyer's nitric acid, standing at 66° to 68° Twad.
Engraver's acid " 80° Twad.

The highest strength at which it can be obtained is about 100° Twad., or 1·50 specific gravity; but this is not reached in the ordinary manufacture.

The wholesale price varies, according to quality, from $2\frac{1}{4}d.$ to $4\frac{1}{2}d.$ per lb.

Fig. 2.



The crude sulphate, called "nitre cake," left in the retort, gives the following analysis, taken from a large number of samples:—

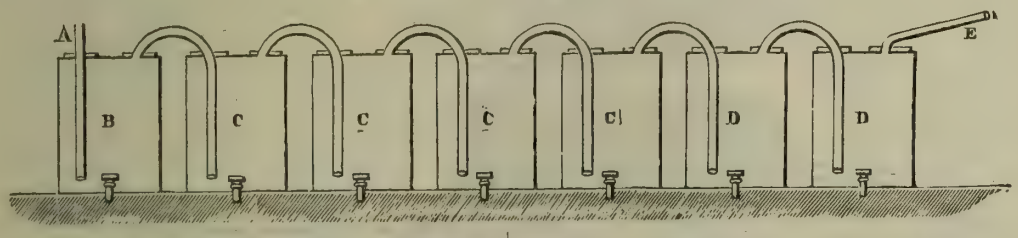
Sulphate of soda,..	78·80	75·09	81·37	71·08
Free sulphuric acid,	14 78	16·61	12·22	21·20
Water,.....	3·22	6·10	4·11	5·51
Sand and insoluble,	3·20	1·20	2·30	2·41
	100·00	99·00	100·00	100·20

—(R. C. CLAPHAM.)

But by far the largest quantity of nitric acid is produced in this country during the manufacture of sulphuric acid in alkali and manure works.

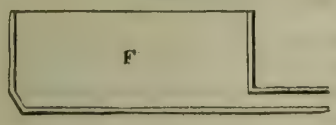
In this operation the nitre pot, F (Fig. 4), in which the mixture of nitrate of soda and sulphuric acid takes place, is fixed at the end of a range of pyrites burners, so that the heat of the burners can be utilized in heating the pot. A charge of from 1 cwt. to 2 cwts. is put in the pot, in accordance to the number of burners at work. The heat is regulated and must be kept moderate, so that the decomposition is gradual

Fig. 3.



and spread over a certain number of hours. The heat at which the mixed gases of nitric and sulphurous acids pass into the leaden tower, called a "Glover tower," may be said to be about 250° Fahr., depending on the number of burners. At one time the whole of the nitrous acid gas, after performing its chemical functions in the chambers, was allowed to pass out into the atmosphere, and was wasted; and it also proved very destructive to animal and vegetable life. But since the nearly universal adoption of the GAY-LUSSAC towers, by which the escaping nitrous acid gas is absorbed by strong sulphuric acid, and by such means made available again for use in the chambers, a saving has been effected in the making of sulphuric acid of more than one-half of the nitrate formerly used. The further description of this process, however, may be considered to belong more properly to sulphuric acid, and will be found under that head.—(R. C. CLAPHAM.)

Fig. 4.



NITRO-GLYCERINE.—Nitro-glycerine was discovered in 1847 by SOBRERO in Paris, who obtained it by acting with nitric acid on glycerine, and called it, on account of its explosiveness when the temperature is suddenly raised, *pyro-glycerine*. At first it was put to no practical use; later it found pharmaceutical application, chiefly in America, under the name of *glonoïn*. Its value as an explosive was demonstrated by ALFRED NOBEL in 1863.

Nitro-glycerine is, according to WILLIAMSON, a compound ether of glycerine, a glyceride of nitric acid, or a glycerine trinitrin; the hydrogen atoms

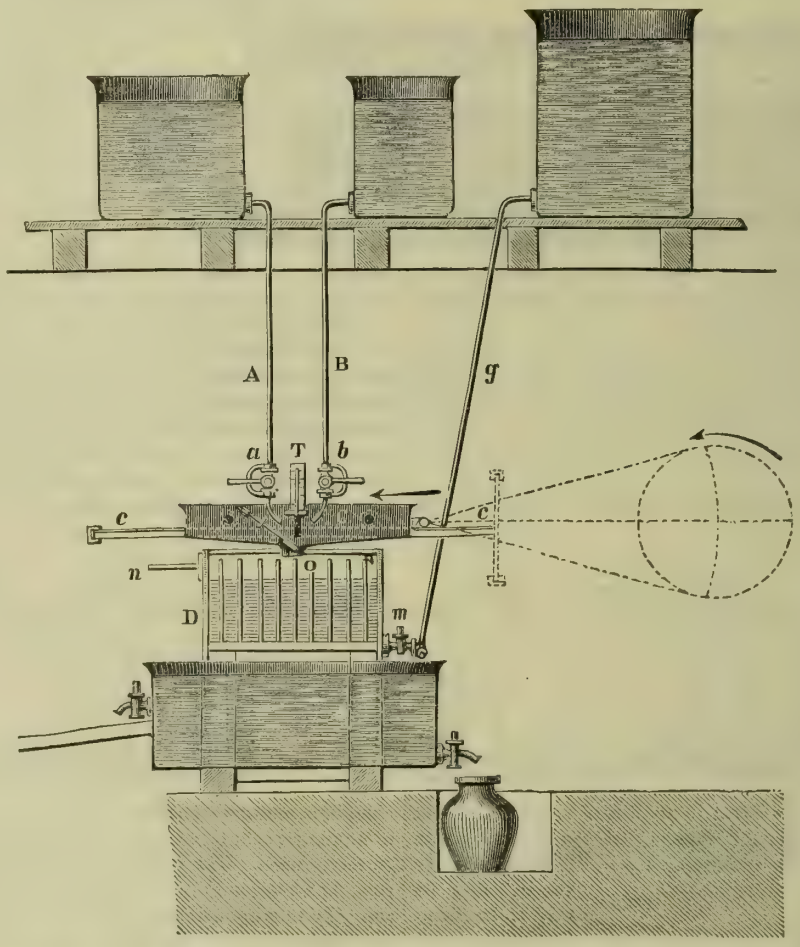
of the three hydroxyls of glycerine being replaced by the radical of nitric acid. Its formula, $C_3H_5N_3O_9$, resolves itself into $\left.\begin{matrix}CH_2.O.NO_2\\CH.O.NO_2\\CH_2.O.NO_2\end{matrix}\right\}$ But the nitro-glycerine of commerce is rarely, if ever, pure glycerine trinitrin; it contains, according to HESS, more or less quantities of glycerine mononitrin and glycerine dinitrin. HESS found 13·7 to 16·6 per cent. of nitrogen in commercial samples, whilst pure glycerine trinitrin requires 18·5 per cent. of nitrogen.

Nitro-glycerine is formed, as already stated, through the action of concentrated nitric acid on glycerine. The process is represented by the equation—

Glycerine.		Nitric Acid.		Nitro-glycerine.		Water.
$C_3H_5(OH)_3$	+	$3NHO_3$	=	$C_3H_5(O.NO_2)_3$	+	$3H_2O$.

By using a mixture of nitric and sulphuric acids, the latter binds the water eliminated in the reaction; and by thus preventing a dilution of the glycerine, aids the formation of the nitro-glycerine.

According to SOBRERO, 2 volumes of sulphuric acid, of 1·831 specific gravity, and 1 volume of nitric acid, of 1·525 specific gravity, are mixed, permitted to cool, and into this mixture half a volume of



glycerine, of a syrupy consistency, is introduced with constant stirring. The mixture is again cooled, not necessarily below 0° C.; and, after having become turbid and been separated into two layers, poured into fifteen to twenty times its bulk of cold water. The oily nitro-compound sinks quickly to the bottom, is freed of unchanged acid and glycerine through repeated washing with water, and, lastly, dried *in vacuo*.

PRAEGER and BERTRAM add 1 part by weight of glycerine to 8 parts of a mixture of 1 part of concentrated nitric acid and 2 parts fuming sulphuric acid. LIEBE recommends to pour 1 part by weight of glycerine into a mixture of 2 parts of nitric acid, of 1·525 specific gravity, and 4 parts of concentrated sulphuric acid, to keep the mixture below 25° C., and to dry the washed nitro-glycerine in the steam bath. Various other methods have been proposed.

In preparing nitro-glycerine on a large scale, the glycerine is obtained from some candle factory, the sulphuric acid, likewise, from some outside works, but the nitric acid is produced on the spot. The nitro-glycerine works must be so placed that, in case of an accident, the destruction should be limited

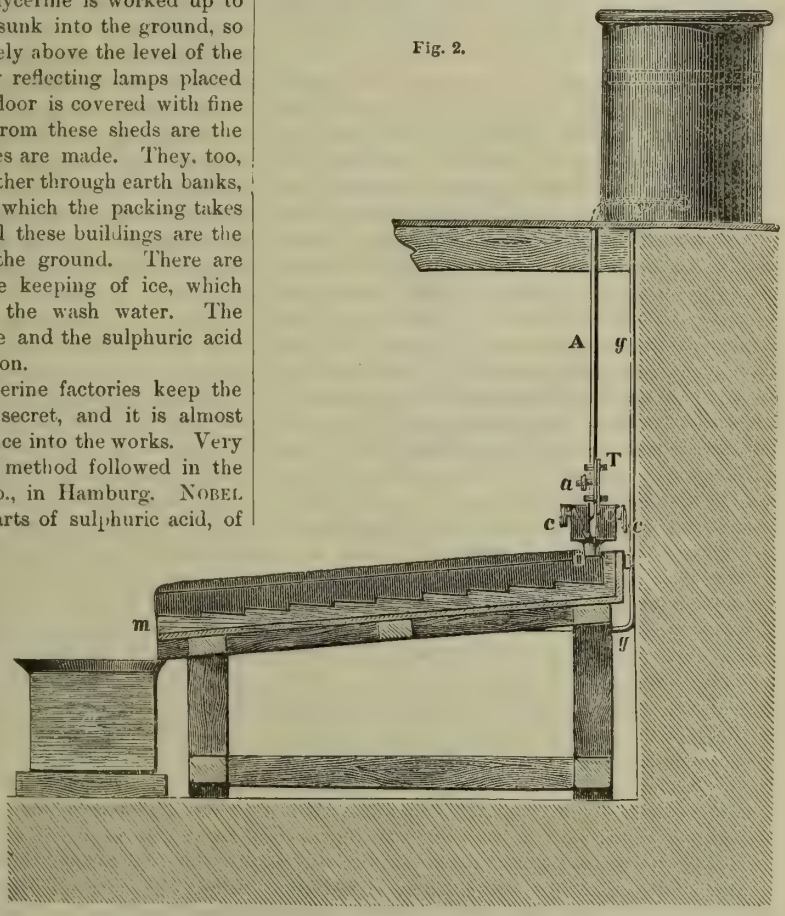
to the factory. The nitric acid is distilled in a compartment by itself. The manufacture of the nitro-glycerine usually takes place in three wooden sheds of light structure, separated from one another by strong earth banks, of 25 to 30 feet in thickness at their base; the walls and roofs are lined with straw, and the temperature, by means of hot water pipes, is kept day and night at 15°.

In the one shed the glycerine is brought together with the mixture of acids; in the second shed the nitro-glycerine is poured into the water, and otherwise washed; in the third shed the complete elimination of acid from the oily compound is effected, and eventually the nitro-glycerine is worked up to dynamite. The sheds are sunk into the ground, so that their flat roofs are barely above the level of the ground; they are lit up by reflecting lamps placed outside on the roofs; the floor is covered with fine sand. At some distance from these sheds are the huts in which the cartridges are made. They, too, are separated from one another through earth banks, and so is another shed in which the packing takes place. Quite away from all these buildings are the store houses, sunk into the ground. There are usually also cellars for the keeping of ice, which latter serves for cooling the wash water. The storing of the raw glycerine and the sulphuric acid requires no special precaution.

As a rule all nitro-glycerine factories keep the details of their processes secret, and it is almost impossible to gain admittance into the works. Very little is known of the exact method followed in the factory of A. NOBEL & Co., in Hamburg. NOBEL states that he pours 3·5 parts of sulphuric acid, of 1·83 specific gravity, on 1 part of potassic nitrate, cools the mixture to 0° C., separates the hydro-potassic sulphate, which crystallizes out from the mixture of acids, and introduces drop by drop into this latter the glycerine. After a short time the nitro-glycerine has been formed; the mixture is then transferred into cold water, and the process continued as mentioned before.

A continuous process, and one said to be free from danger, was recommended in 1868 by RUDBERG, in Stockholm. Figs. 1 and 2 show, respectively, vertical sections of front and side views of the apparatus employed. Vessel 1 contains the acid mixture which had previously been cooled in a vat lined with lead; vessel 2 contains the glycerine, and 3, cold water. All these have outlet tubes which are provided with taps. The contents of 1 and 2 are permitted to flow, on opening the taps *a* and *b*, through the tubes A and B, into the vessel provided with the funnel, C; this latter vessel is suspended over the channel, D, which is fitted with stair-like shelves, and surrounded by a water-tight wooden trough. According to the arrangement represented in Fig. 1, the vessel receiving the contents of 1 and 2 is not suspended, but is provided with wheels, so that it can be caused to move continuously to and fro on the rails, *c*, as may be gathered from the dotted lines. The lower ends of the outlet tubes, A and B, are slightly bent, and are situated at the opposite side of the bulb of a thermometer, T, placed between them. In this way the glycerine and the acid mixture meet just below the thermometer, and the rise of temperature caused by the chemical reaction can thus be accurately measured. For greater caution sake, there is a second thermometer fixed in the tube of the funnel, C. The water from 3 enters through tube *g* by tap *m*, the space between the channel, D, and the surrounding trough, and finally leaves through tube *n*.

Fig. 2.



The working of the apparatus is easily understood. The channel, D, is surrounded with cold water from 3, through *g* and *m*, and now the acid mixture is allowed to flow slowly into the funnel, C, which is set into oscillating motion, so that the tube of the funnel should alternately be over the different compartments of the channel, D. As soon as the acid begins to run simultaneously from all the compartments, the glycerine is turned on and allowed to mix with the acid. The reaction between the two takes

place immediately; it is completed as soon as the mixture has passed through the channel, D, which is carefully to be kept cool by constant supply of cold water. From D the mixture flows into the large vat, 4, where the nitro-glycerine separates as an oily layer. It is drawn off, washed first with solution of sodium carbonate, then with water.

The remaining diluted acid can be concentrated with very little expense, and used again for nitrifying glycerine. If no such re-application of the acid mixture is intended, the vessel, 4, is filled with water, whereupon the nitro-glycerine sinks to the bottom, and can easily be separated from this supernatant acid liquid. Washing with sodium carbonate solution and with water conclude the process, as before.

PELLET and CHAMPION noticed in 1871, that if the whole quantity of glycerine required in one operation be suddenly poured into the acids, and the mixture stirred with a glass rod for ten seconds, the formation of the nitro-glycerine will have been completed, and yet there has been no time for a rise of temperature to take place; on throwing, therefore, the mixture into a large mass of water, the nitro-glycerine will separate. But the syrupy condition of glycerine makes it difficult to let a quantity of it flow quickly into the acid; CHAMPION recommends, therefore, to allow the glycerine to run down the sides of the mixing vat, so as to accumulate on the surface of the acids, and when the desired quantity is floating above the acids, to mix the two quickly with a glass rod for ten minutes, and then to pour the mixture into fifteen to twenty times its bulk of cold water. Washing with soda and water, and drying by means of calcium chloride, or by heating to 30° to 40° C., conclude. The quantity of nitro-glycerine thus obtained is double that of the glycerine used.

In a dynamite factory on the Continent, in which the daily production surpasses 2 tons, the nitro-glycerine is, according to F. CAPITAINE, prepared in the following manner:—The glycerine used comes from Marseilles, is of 1·25 to 1·26 specific gravity, green-brown, contains undecomposed fats, and freezes occasionally in winter. The nitric acid is obtained by distilling a mixture of equal parts of Chili saltpetre and sulphuric acid in cast-iron retorts of about 180 cubic feet contents; it is red from nitrous acid, and contains also chlorine, derived from chlorides in the saltpetre; but it can, nevertheless, be employed without further purification for the nitrification of the glycerine. The nitric acid is brought to the specific gravity 1·48, and 1300 lbs. of this acid are mixed in four cast-iron pans with twice that weight of sulphuric acid; this mixture, which is left to cool for a day, serves for the treatment of 630 lbs. of glycerine. The acid is drawn from the pans into a wooden cylindrical vat, of about 6 feet height and 3½ feet diameter, lined inside with thick lead, and containing along its lining two spiral lead pipes, of about 1 inch diameter, which reach from the bottom to the top. Each of these spirals, or worms, forms a system by itself, through which cold water circulates, and one may serve as substitute for the other, in case of accident. The mixture of acids is stirred first by itself in this vat; the stirring is effected by two iron discs, covered with lead, disc and covering being perforated, which glide up and down on a vertical iron shaft, the gliding motion being effected by pulling the rope attached to the discs over a pulley; the two or three workmen who perform this task stand at a distance of 30 to 40 feet from the vat behind a strong earth bank. When the acids have been introduced into the vessel, and the agitation has commenced, water of 6° to 8° C. is let into the worms; the temperature of the acid can in this way be maintained at 14° to 16° C., as may be ascertained from a thermometer which reaches through the lead cover of the vessel into the acid. The glycerine, which is kept in a zinc tank on the roof of the shed in which the mixing vat is, is now allowed to run into the latter vessel. The flow is regulated by means of a tap, and also by letting the glycerine first run into perforated zinc boxes, placed on the lid of the mixing vat, and corking up, if occasion requires, some of the perforations. As soon as the glycerine falls into the acid the temperature rises at once; but by carefully regulating the supply of glycerine it may be kept at 18° C., or lower. It is advisable not to allow the temperature to rise above that degree, though experience shows that a higher temperature yields a larger quantity of nitro-glycerine. It requires, according to the season and the temperature of the cooling water, one half hour to two and a half hours for 630 lbs. of glycerine to pass into the mixing vat; the stirring must not be stopped for a moment during the process. When all the glycerine has been added to the acids the mixture is at once drawn off through a leaden pipe to the so-called wash shed, where it passes into a tank about 8 feet high and 12 feet diameter, which is half filled with cold water. The inlet tube carries a sieve, to retain lead sulphate that may have been brought from the mixing vat. Whilst the nitro-glycerine flows in, stirring with wooden poles is begun, and continued until the nitro-compound has settled below the dilute acid. The bottom of the wash vessel is slightly inclined, so as to allow a complete drawing off of the nitro-glycerine. The outlet taps are of stone-ware. The nitro-glycerine is now twice washed with water, freed from acid and lead sulphate, and finally washed with water to which some sodium carbonate has been added.

But even after this purifying process there remain traces of acid; to eliminate these the nitro-glycerine is transferred to a third shed, where it is agitated for about an hour in a rotating vessel called the *butter-machine*, with about 50 lbs. of a concentrated solution of sodium carbonate; after this time it will no more redden litmus paper. It is now separated from the alkaline solution, filtered through felt, and collected for further use in leaden reservoirs.

The yield by this method is from 950 to 1200 lbs., according to the condition of the raw glycerine, the concentration of the acids, and the temperature.

It is considerably below the theoretically calculated quantity. This shortcoming is due to the formation of glycerides, which dissolve in the wash waters. As a rule, the yield in winter is greater than that in summer.

At G. M. Mowbray's factory near North Adams in Massachusetts, United States, the nitric acid is distilled from five retorts, each of about 100 cubic feet contents, which are placed in a well ventilated building; each retort receives 300 lbs. of Chili saltpetre, and 375 lbs. of sulphuric acid; the vapours pass through stoneware pipes into a series of four receivers, likewise of stoneware, and placed on a bank about 1 foot above the ground; the first two receivers contain each 150 lbs. of sulphuric acid, the third 100 lbs., the fourth nothing. The sulphuric acid in the receivers facilitates the condensation of the nitric acid vapours, and the mixture of acids required for the nitrification of the glycerine is obtained at once. The distillation is finished after twenty-four hours; the mixture of acids, altogether about 600 lbs., is then drawn off into carboys, and from these emptied into a stone trough, which is capable of holding the contents of 18 carboys. In order to effect a uniform mixing of the acids, and also to remove nitrous gas, a current of air is passed for five minutes through the liquor in the trough.

The nitrification of the glycerine takes place in stoneware jars; 116 of these are distributed over nine wooden troughs, which latter are filled to within a few inches from the top of the jars with ice-cold water, or a mixture of ice and salt. Each jar receives 17 lbs. of acid mixture, and into this 1 lb. of glycerine is introduced drop by drop from glass vessels, which are placed on a shelf just above the acid jars. Below this shelf runs an iron tube, about 1½ inch wide, through which cold dry air is conducted; from this tube glass pipes branch off (joined by means of india-rubber tubes) into each jar, which thus receives during the dropping-in of the glycerine a constant current of cold air, acting both as cooler and as stirrer. Very beneficial influence is ascribed to this air current, which oxidises also nitrous acid vapours.

The introduction of the glycerine into the acid must be finished within one and a half hour; there should be no rise in temperature, and certainly no appearance of red vapours. After the transformation of the glycerine, the jars are emptied into troughs containing water of 21° C.; the nitro-glycerine sinks to the bottom and remains covered with about 6 feet of water, for a quarter of an hour, when first the water is drawn off from above, then the nitro-glycerine from below. The latter is transferred to oscillating casks, in which it is washed three times with water, and twice with soda solution, a current of air passing through the liquid all the time. The wash-waters pass into a tub, from thence into two casks, sunk into the ground, where such nitro-glycerine as had been carried away by the water is retained.

The nitro-glycerine is carried in copper vessels to a shed, about 100 yards distant, and poured into stoneware jars, of 60 lbs. contents, and the jars placed into reservoirs filled with water of 21° C., and left here three days. Impurities rise to the surface, and are skimmed off.

The nitro-glycerine is now ready for commerce. It is filled in canisters of galvanized sheet iron, coated inside with paraffin, and capable of holding 56 lbs.; the floor of the shed where the filling takes place is covered with a thick layer of calcined plaster of Paris, in order that any spilt nitro-glycerine be absorbed at once. The canisters are then exposed to the cold of ice and salt for the sake of freezing their contents; in this state they are stored, thirty to forty to a batch, in magazines at least 100 yards from all the other buildings of the factory. The transport of this nitro-glycerine takes place also whilst it is frozen.

The average yield in Mowbray's factory amounts to 223 per cent of the glycerine employed.

Properties.—Nitro-glycerine is at ordinary temperatures an oily liquid, clear, colourless, or yellowish, refracting light, of sweetish and burning taste, without odour, of 1·6 specific gravity; at lower temperatures it becomes solid, the degree at which it solidifies greatly varying. Champion's was at —15° C. syrupy, but becomes solid after continued keeping at —20° C.; Mowbray's solidified at 7·20 C., and contracted by $\frac{1}{12}$th of its bulk; Nobel's nitro-glycerine became solid at 12·8° C., and expanded. In water it is insoluble, but dissolves easily in ether, wood spirit, benzol, chloroform, and hot alcohol.

It produces serious consequences when taken into the system—vertigo, weakening of sight, stupor, pains in the cardial region; in larger doses it acts like strychnine, being fatal when more than 10 grams. are swallowed. Even mere contact with the skin produces serious symptoms, though workmen get used to it after a time.

Pure nitro-glycerine does not decompose spontaneously at ordinary temperatures, but at higher temperatures nitrous acid vapours are disengaged. It may be heated to 100° C. without danger; it may even, according to E. Kopp, be evaporated by being dropped upon a moderately hot plate; but if the plate is hot enough to bring the nitro-glycerine to boiling, it explodes, according to Gorup-Besanez. Experiments of Champion have shown that it evaporates at 185° C., boiling and evolving red fumes, burns briskly at 217° C., and detonates with violence at 257° C.

The decomposition of exploding nitro-glycerine takes place, as Berthelot's researches show, according to the equation—

$$2C_3H_5(ONO_2)_3 = 6CO_2 + 5H_2O + N_6 + O.$$

Nobel calculates that 1 volume of nitro-glycerine disengages 1298 volumes of gases of 100° C. at a barometric pressure of 760 m.m., which consist of 554 water vapour, 469 carbonic acid, 236 nitrogen, and 39 oxygen. List estimates the bulk of the liberated gases at 1504·9 volumes. Nitro-glycerine evolves therefore, at the lowest estimate, nearly six times

as much gas as gunpowder, computed for a temperature of 100° C.; but a far higher degree of heat is produced by the instantaneous combustion of nitro-glycerine, which, according to Nobel, expands the bulk of the freed gases to eight times of the original 1298 volumes, whilst the gases of gunpowder would not be trebled at a like temperature; the explosive force of nitro-glycerine therefore stands to that of gunpowder as 13 to 1, according to volume.

Putting a light directly to nitro-glycerine does not lead to detonation. Poured out in a thin layer, the liquid burns away like gunpowder. A red-hot iron rod, applied by Nobel to nitro-glycerine, had no effect whatever; a burning wooden splinter kindled it to a quiet flame; but on removing the match, the flame of the nitro-glycerine went out immediately. There is no danger, therefore, if any amount of nitro-glycerine is set on fire; it will burn away quietly long before it is heated to the degree at which it explodes. It is only on being heated in a closed space that its entire mass explodes, when the temperature reaches 257°. Such a heating can be effected by the electric spark. Professor Abel placed two poles, connected with a Ruhmkorff coil, into some nitro-glycerine, and allowed a number of sparks to pass between them: the surface of the nitro-glycerine became agitated, turned black, and after half a minute exploded.

Gradually increasing pressure is unable to explode liquid nitro-glycerine; but a sudden blow will do it, though it detonates only that portion with which it came in direct contact. The explosion produced in the part that had been directly exposed to the blow will not propagate itself to the rest of the nitro-glycerine. If, however, nitro-glycerine is in a solid condition—frozen, for instance—a blow given to a portion will be transmitted at once to the entire mass. Several accidents are on record where the explosion could be traced to some mechanical force having acted on frozen nitro-glycerine. One kind of mechanical force—shaking—seems to form an exception to this observation; for, as already mentioned, Mowbray's nitro-glycerine is safer to move in a frozen than a liquid state, and Nobel also maintains that liquid nitro-glycerine is extremely sensitive to vibration.

The detonation of gunpowder, gun-cotton, or fulminate, causes nitro-glycerine to explode, whether it is loose or shut up.

Exposure to the solar rays transforms nitro-glycerine into a very unstable, easily explodable substance; and Jouglet observed spontaneous explosion of nitro-glycerine in air charged with ozone.

Application.—The earliest application of nitro-glycerine was in conjunction with gunpowder; the latter was exploded by any of the usual methods, and through its explosion the nitro-glycerine. A tin cartridge was filled first with gunpowder, then with nitro-glycerine, closed by a cork, and placed into the bore-hole, which had to be about one-quarter of an inch wider than the cartridge; the space between was filled up with coarse-grained gunpowder, which covered the cartridge about 1 inch high, a fuse was inserted, and the bore-hole tamped with sand.

Later a special detonating capsule was used by Nobel, consisting of a wooden box filled with fine powder, and provided with a fuse. The nitro-glycerine was poured directly into the bore-hole, which had to be lined with plastic clay.

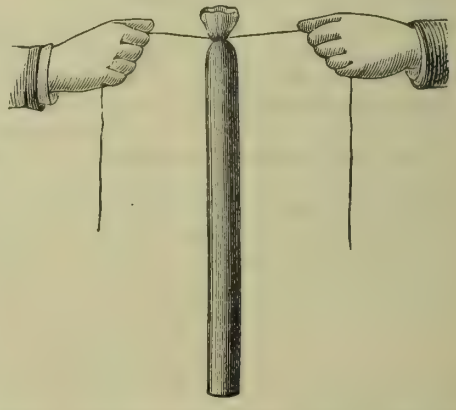
In March, 1865, blastings on a large scale were carried out in the granite quarries near Stockholm A bore-hole of about 10 feet in depth was charged with 5 lbs. of nitro-glycerine; after explosion about 200 cubic yards of granite, weighing something like 350 tons, had been found torn away, and the main rock was traversed by long fissures. This result created much sensation, and caused a great demand for the new explosive. The application of nitro-glycerine increased in the next following years, and it was, amongst others, soon used for breaking up large masses of old iron, such as anvils, cylinders, &c.

The efficacy of nitro-glycerine in water was shown by experiments which Nobel performed in 1866 in a pond near Hamburg. A canister, containing about 2½ lbs. of nitro-glycerine, was lowered under the surface of the water and fired; the explosion sent up a column of water of about 9 feet in diameter to a height of above 300 feet. A like quantity of gunpowder in a similar canister lifted, on firing, the water to not more than a few feet.

The following directions were given by Nobel for the best way of applying nitro-glycerine:—

It is best to use narrow bore-holes; their depth and number varies according to requirements. The nitro-glycerine may be poured into the bore-hole itself if the surrounding material is not absorbent or leaking; but, on the whole, it is most advisable to introduce the nitro-glycerine in cartridges. These cartridges are of paper, and can be obtained in different sizes, or they may be made at the place where the nitro-glycerine is to be used. The annexed Fig. 3 explains the mode of filling and tying them.

Fig. 3.



Deep bore-holes may receive two or more cartridges. If the bore-hole is vertically descending,

the cartridge is introduced by gently pushing it down with a wooden rod. The firing is effected by means of a second cartridge, only 2 or 3 inches long, which is partly filled with powder, *d*; the fuse is placed into the powder, and the remaining space of the cartridge is filled up by paper, *c*, and soft clay, *b*, in order that the explosion of the gunpowder should produce a blow upon the nitro-glycerine, which would not detonate through the flash of the powder alone. Thus prepared, the powder cartridge is placed on the nitro-glycerine (Figs. 4 and 5). Where the bore-hole runs upward the cartridge is introduced with its tied end uppermost, and it is then fixed in its

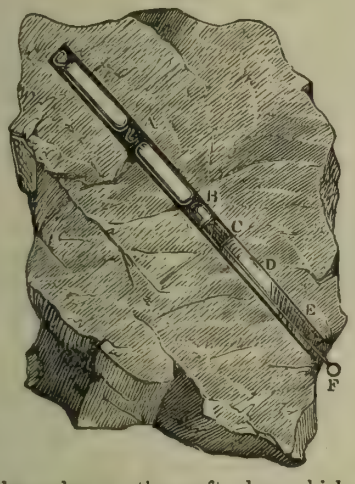
Fig. 4.



Fig. 5.



Fig. 6.



position by a clay or other soft plug, which spreads out in the bore-hole, and thus supports the cartridge (Fig. 6).

After the introduction of the cartridge the bore-hole must be filled up loosely with dry sand, or, if the bore-hole proceeds from below upwards, with soft clay plugs, which had been rolled in dry sand. A hard plug is to be avoided, except above the powder cartridge, where the sand or clay may be tightened by gentle pressure; a loose plugging above the powder would prevent the gases evolved in the firing of the powder acting upon the nitro-glycerine. In watery bore-holes the paper cartridge, filled with nitro-glycerine, is placed with its end open, into which a wire covered with gutta-percha and provided with a patent cap is introduced, so that the latter reaches only 1 inch into the nitro-glycerine. The connection between wire and cap must be well covered with tallow or pitch; the hole is then filled up with water.

Rudberg fires the nitro-glycerine in a bore-hole by a blow, which raises the temperature and thus produces detonation. To effect this he closes the mouth of the bore-hole, which had been partially filled with nitro-glycerine, with a wooden plug, on which he places a second one, the upper end of which is above the mouth of the hole, and to which a powerful concussion is applied by means of a vertically falling ram, or a beam which can be deprived of its equilibrium by pulling a cord attached to it properly. According to another method of the same inventor, the bore-hole (Fig. 7), after being filled to a certain

Fig. 7.

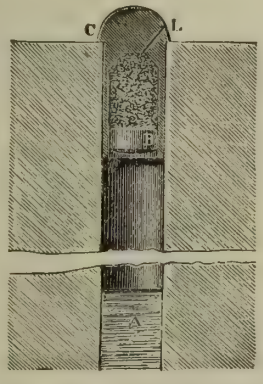
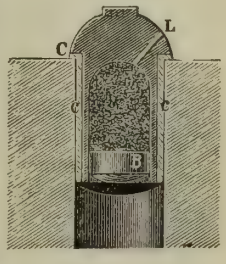


Fig. 8.



height with nitro-glycerine, is closed with a tube, the lower end of which is surrounded with hemp and fits thus hermetically, whilst the upper end, C, standing out from the hole, is closed and filled with gunpowder, and below this a plug, B; on firing the powder by means of the sulphur fuse through the spundhole, L, the plug, B, is violently pushed down upon the nitro-glycerine and explodes it. For the sake of better closing, a sort of cap, *c* (Fig. 8), is placed on the bore-hole; into the cap fits the loaded tube, C. The nitro-glycerine may also be first filled into narrow zinc cylinders, closed with plugs, and thus be placed into the bore-holes; they are let down by means of an attached string, which is withdrawn before firing.

The highly favourable reports on the explosive value of nitro-glycerine were soon followed by statements of its being one of the most dangerous of known blasting agents. In 1866 a West India mail packet was blown up, a wharf torn down, a number of adjacent ships were injured, and many lives lost at Colon, through an explosion of nitro-glycerine. Not long after that a fearful accident occurred in San Francisco by the dropping of a box containing the same material. Later on, a Newcastle magistrate and several other persons fell victims to an accident with this explosive body. In 1868 a factory at Stockholm where nitro-glycerine is manufactured was blown up and a number of men killed, and not long after that an explosion attended with fearful loss of life occurred in Belgium. This last-named accident led to the authorities altogether prohibiting the use of this explosive compound in that kingdom.

The exact cause of these fatal explosions was never ascertained, but general opinion ascribed them to

violent concussion of the liquid nitro-glycerine, and to a spontaneous decomposition of the latter. Mr. NOBEL thinks that the manufacturers were not aware at the time of the immense influence which the metallic packing then used (tin canisters) exercises, even when inclosed in wooden boxes, on the liability of nitro-glycerine to explode by concussion.

It was then proposed, and adopted as a temporary measure, to render nitro-glycerine inexplosive, or rather much less sensitive, by adding methylic alcohol, which it readily dissolves. On shaking it with water, which takes up the alcohol, the explosive properties are fully restored, and the same detonator-cap, which has not the slightest effect on the mixture of nitro-glycerine and wood naphtha, explodes it after a moment's washing with water.

Fig. 9.



The separation of the nitro-glycerine from its solvent is effected in glass bottles of a construction represented in Fig. 9. It is filled with the solution up to C, then with water to B, allowing a space of A to remain free. The top is then closed, and the bottle several times shaken; when after this the nitro-glycerine has been separated, the bottle is turned upside down, the tap is opened for the inflow of air, and the nitro-glycerine issues from the small side tube in the cork. These bottles are from designs by NOBEL & Co., and may be had in Hamburg at two shillings each.

That method of protection, although much patronized by chemists, had many drawbacks, and was troublesome for miners to adopt. It was in June, 1867, superseded by the invention of dynamite.

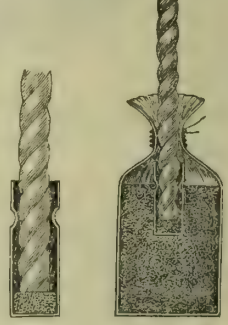
DYNAMITE consists of nitro-glycerine absorbed in porous substances, particularly a siliceous infusorial earth, occurring in Hanover, called "Kieselguhr." It is erroneously believed that it was discovered accidentally through a leakage of nitro-glycerine which had run into porous silica, known under the name of "kieselguhr." The first dynamite made contained no silica; it consisted of porous charcoal and nitro-glycerine, and numerous experiments were made with various absorbents, such as porous terra-cotta, sawdust, ordinary paper and nitrated paper soaked in the liquid explosive and rolled into cartridges, before porous silica was finally adopted. Kieselguhr absorbs from three to four times its own weight of nitro-glycerine, and possesses the advantage over other absorbents of resisting a greater degree of pressure without parting with any of the nitro-glycerine which it holds. At first the new blasting agent made but slow progress, owing in a great measure to the strong prejudice existing against its chief ingredient. But gradually it has grown into favour, and numerous dynamite factories have sprung up, of which no less than fourteen are under the inventor's control.

The cost of the raw materials (1·15 ton of highly concentrated nitric acid, 2 tons of extra strong sulphuric acid, 9 cwts. of glycerine, and 5 cwts. of dried kieselguhr for every ton of dynamite), together with the packing, represented at the opening of the dynamite trade one-half, and represent now three-fourths of the nett price charged by the German factories. In Great Britain a considerably higher selling price leaves less profit to the manufacturers, owing to the great stringency of the law and the extraordinary difficulties and expenses connected with the transit and storing of nitro-glycerine compounds.

The infusorial earth, to be employed as an absorbent, must be freed from organic admixtures, water, and coarse siliceous grains. The first two are eliminated by calcination, which is carried out in furnaces situated one above another, usually four of them; the kieselguhr is pushed from the uppermost to the lowest. The calcined mass is then crushed between cylinders and passed through wire sieves.

The saturation of the infusorial earth with the nitro-glycerine takes place in the same building in which the liquid is finally washed. According to F. CAPITAINE, 50 lbs. of kieselguhr are put with treble the weight of nitro-glycerine into flat wooden trays and well mixed by hand; the workmen ought to have gutta-percha gloves, but they mostly neglect this precaution. In about half an hour the mixing is accomplished; the mass is now pressed by hand through sieves, and is ready for being filled in cartridges. The cartridges are, like those for liquid nitro-glycerine, of cardboard paper or of vegetable parchment; their mode of filling is like that described in the case of nitro-glycerine. For larger charges of dynamite zinc canisters are used.

Fig. 10. Fig. 11.

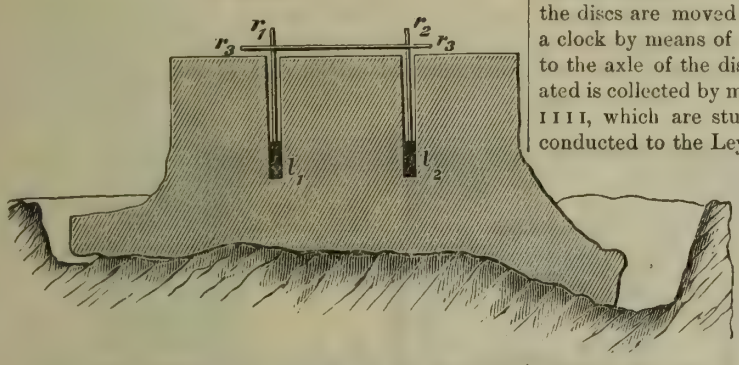


The detonator, or exploder, contains a charge of fulminate of mercury. NOBEL'S detonator is represented in Fig. 10; and Fig. 11 shows the mode of insertion in the dynamite cartridges.

The firing of a cartridge is now generally accomplished by the electric spark. Before proceeding to describe this mode, a method which had been recommended by TRAUZL may be mentioned. It rests on the fact that the explosion of dynamite proceeds with great rapidity, even if the charge is of a small diameter. In Fig. 12 l_1 and l_2 are bore-holes in a tree stump, charged partially with dynamite: r_1 and r_2 are paper cylinders filled with dynamite, which are sunk into the holes with their upper ends protruding. The bore-holes are now plugged up in the usual way. A third thin paper cylinder, r_3 r_3, filled with dynamite is now laid across the two others, and tied to them with string at the crossing places. On placing now the detonating cap in any end of these cylinders, and firing it,

both charges will explode simultaneously. Thus the dynamite in the paper tubes serves as a fuse.

Fig. 12.



It is even possible to fire one charge of dynamite by means of the violent vibration produced by the explosion of another. Thus, if two charges are connected by a metal tube, such as an ordinary gas-pipe, and the one is exploded, the second will go off simultaneously.

But the most rational means of exploding dynamite is by electricity. Among the electrical machines in use for this purpose, the one constructed by Bornhardt, in Brunswick, and represented in Figs. 13, 14, 15, and 16, receives special attention from Trauzl and other authorities on blasting operations. The electricity is produced by the friction of the ebonite discs, F F, between the fur padding, R R; the discs are moved in the direction of the hand of a clock by means of the handle, *d*, which is attached to the axle of the discs. The electricity thus generated is collected by means of the four collecting rings, I I I I, which are studded with points, and at once conducted to the Leyden jars, L L, that is to say, the jars are charged. The ring, D, is in metallic connection with the exterior coating of the jars; the ring, C, with the lever, G. On pressing the knob, K, the lever, G, turns round its fulcrum (as indicated by the dotted lines in Fig. 13), and the point, G, touches the common knob of the jars, coming thus in contact with the interior coating of the jars. If, therefore, C and D are in a closed circuit, pressing of the knob, K, into contact with the Leyden jars discharges the latter. If now a series of explosive charges are by means of metallic wires inserted in the circuit between C and D, and the jars are charged by turning the handle, *d*, 10 to 25 times, according to requirement, these explosives can be fired simultaneously by pressing the knob, K, in the direction

Fig 13.

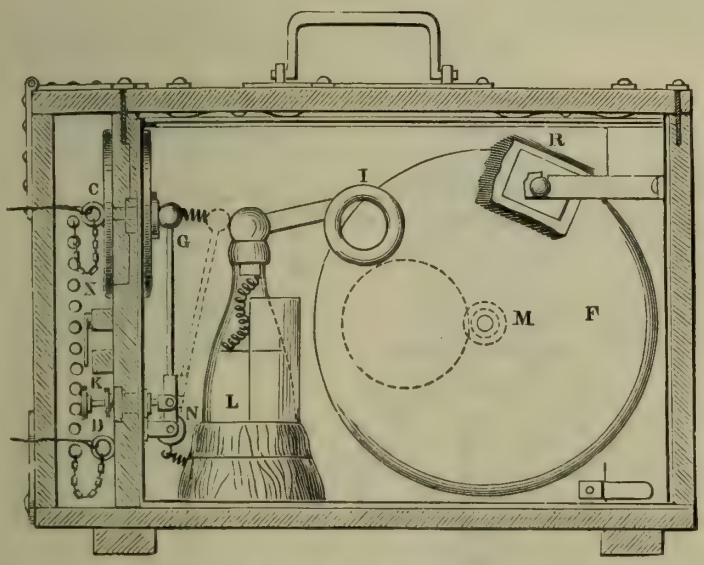
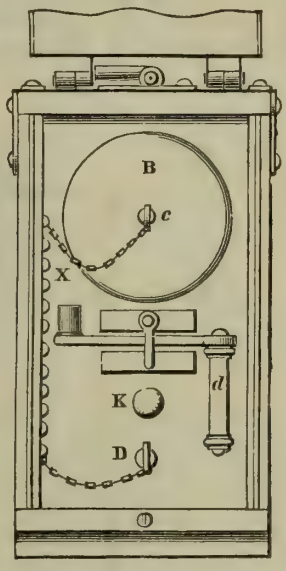


Fig. 14.



mentioned before. It is obvious that this arrangement allows of the firing of the charges at considerable distances from the sources of electricity.

To preserve these machines effective they must be kept carefully dry; for this purpose they are encased in a tin box, into which some hygroscopic substance (calcium chloride) is placed. The box is covered with a glass plate, *g*, and tightly encased in a wooden box, to which the isolated metal eyes, C and D, are attached, and which contains the bearings for the axle, M, and the knob, K. The boxes are not to be exposed for any lengthened time to the rays of the sun.

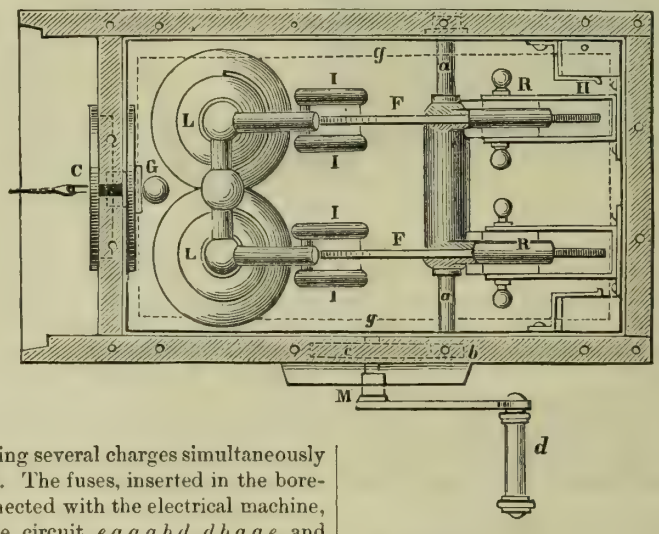
As soon as an explosion has been effected, the circuit wires must be detached from the box, and the handle of the disc taken away by the superintendent of the works. Before connecting the handle all persons employed on the ground should go out of reach of any possible accident.

The fuse (Fig. 17) to be employed in connection with electricity should consist of two wires, *a c* and *b c*, whose ends, *c*, are kept at an unalterable

distance from one another by some insulating mass; of an inflammable mass, *z*, which ignites through the electric spark; of a fulminate, *k*, which is detonated through the mass, *z*, and thus explodes the dynamite charge, into which the fuse is placed; and of an appropriate water-tight wrapper for the inflammable mass and the fulminate; for this last-mentioned purpose cylinders of sheet copper, such as used for ordinary percussion caps, serve very well.

Dynamite is chiefly used for blasting in mines and quarries. The boring of the rocks, the charging of the bore-holes, the firing, &c., is quite similar to that followed in the case of nitro-glycerine. An

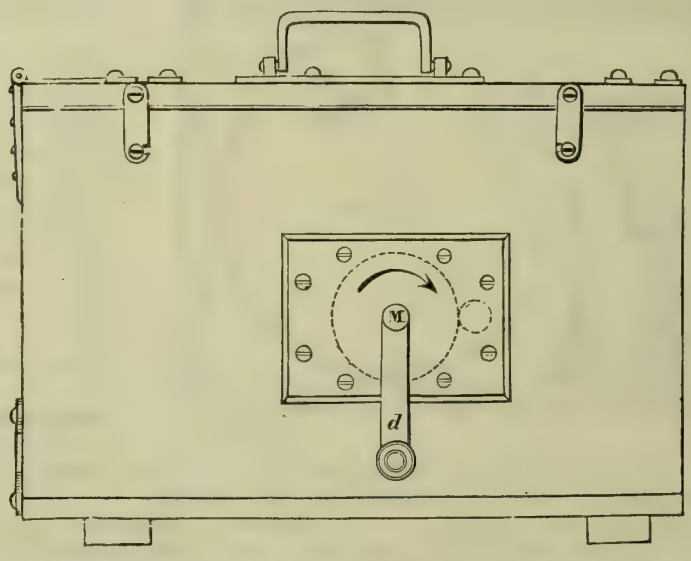
Fig. 15.



arrangement for firing several charges simultaneously is shown in Fig. 18. The fuses, inserted in the bore-holes, *d d*, are connected with the electrical machine, *e*, by means of the circuit, *e a a a b d, d b a a e*, and the fuses are united among themselves and to the conducting wires by the junctions, *c c*.

Rocks under water can be destroyed by applying the dynamite superficially; thus the expense and

Fig. 16.



trouble of boring is saved. In this way several blocks in the harbour of Trieste were removed in 1871. The dynamite was contained in metal canisters, shown in Figs. 19, 20, and 21; the last two are sections, one when empty, the other when charged with the dynamite.

For breaking up heavy ice dynamite seems particularly well adapted. During the siege of Paris in 1870, a canal of more than a mile length was cut into the ice which covered the Seine, for the purpose of allowing free movement to a gunboat that had been frozen in at a spot which was much exposed to the enemy's fire.

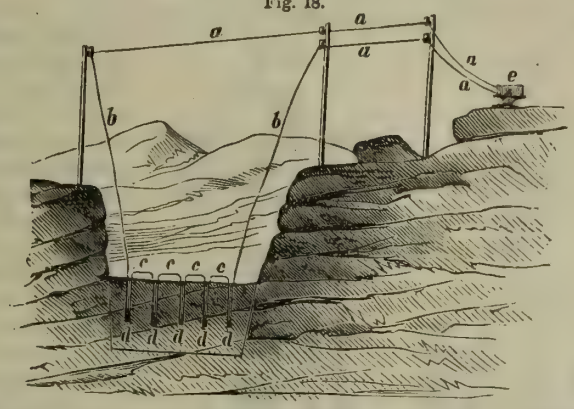
On the Continent dynamite is largely used for

rooting out stumps of trees, for removing stakes from river beds, &c. The mode of proceeding in the latter case, as described by Trauzl, is represented in Figs. 22, 23, and 24. The stakes, twenty-

Fig. 17.



Fig. 18.



four in number, which had to be removed, were imbedded in a branch of the Danube near Vienna.

Fig. 19. Fig. 20. Fig. 21.



The stakes were cut off with the saw just above the level of the water, bored to a depth of about 12 feet, with about one-eighth of an inch in diameter, and each hole charged with 1 lb. of dynamite. The dynamite charges were in tin cylinders, and provided with detonators having electric fuses (Fig. 24). The bore-holes were tamped with water, and the charges were fired by electricity. The explosion brought all the twenty-four stakes simultaneously to the surface, and each stake was completely torn to about 18 inches height from the bottom of the charge. The costs were about one-fifth of what the usual mode of extricating would have been.

A very interesting example of applying dynamite

Fig. 22.

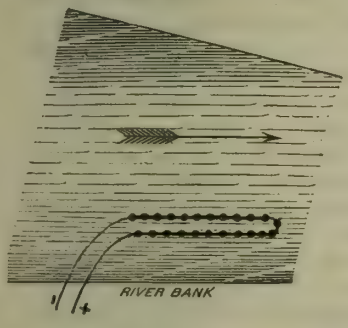


Fig. 23.

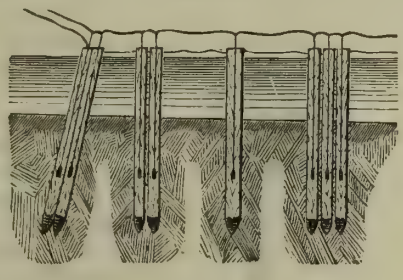


Fig. 24.



to a stump is represented in Fig. 25. It was removed in January, 1874, from the new arm of the Danube near Vienna. The stump measured about 3 feet in diameter at the top, which reached about 20 inches above the water, and was very much rotten. Three holes were bored vertically downwards to depths of $4\frac{1}{2}$ feet, 8 feet, and $8\frac{1}{4}$ feet respectively, with about $1\frac{1}{2}$ inch in diameter. The boring of each of the deeper holes lasted four and a half hours, of the third three hours. Each hole received a charge of 1 lb. of dynamite, packed in water-tight tin cases. The result of the explosion was a complete loosening of the ground in which the stump was embedded, so that its removal by mechanical means was perfectly easy.

Where there is no necessity of removing a stake from below the ground, where it is sufficient to get rid only of such portion as stands in the water, no bore-hole is required; the external application of a dynamite cartridge is enough to effect the removal. The method represented in Fig. 26 was applied in a case where the current of the water was so powerful as to prevent the simple laying on of the cartridge. The latter, *c*, was fastened to a wooden hoop, *b*, of somewhat larger dimensions than the stake, *a*; the hoop was then attached to two strong wooden poles, *d*, *d*, and then pushed over the stake down to the bottom of the river. A cartridge containing 1 lb. of dynamite employed in this manner, broke off stakes of an average diameter of 1 foot.

One of the most recent applications dynamite received is that of breaking up the undersoil for the purpose of enabling the roots of plants of cultivation to draw their nourishment from greater

depths than it would be possible to reach by the aid of the most powerful agricultural machines. The first trials of this kind were made by Dr. VON HAMM, councillor in the Austrian Ministry of Agri-

Fig. 25.

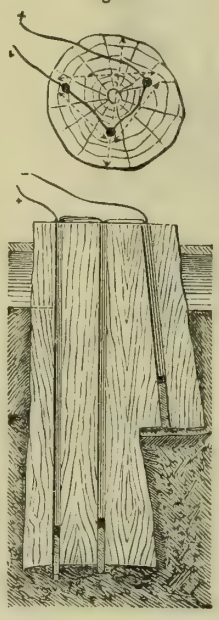
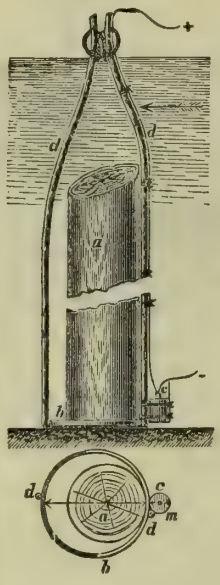


Fig. 26.



culture, at Kloster-Neuburg. A certain extent of arable land was provided with a number of small bore-holes, which were charged with dynamite and exploded. The ground, which had been so hard

Fig. 27.



Fig. 28.



that a stick could not be pushed deeper than 6 inches, was cut up and loosened to such a degree, that the stick could be easily pushed down to a depth of 4 feet at a spot of more than a yard from a bore-hole. To produce these holes a "dibble" and mallet, as shown in Figs. 27 and 28, were used.

Gelatinized Nitro-glycerine.—NOBEL has patented a process for solidifying nitro-glycerine by means of gun-cotton collodion. The explosive compound becomes more and more gelatinous in proportion to the quantity of nitrated cellulose which is dissolved therein; and it forms (when 7 to 8 per cent. of the nitrated cellulose have been incorporated) a solid jelly, which is very safe and highly suitable for every purpose to which very powerful explosives can be applied.

In some explosive liquids (such as nitrate of methyl) collodion cotton readily dissolves at the ordinary temperature, and forms a thick explosive gum or jelly. In the case of nitro-glycerine, however, the incorporation of the above-named gelatinizing substance is facilitated by adding a small quantity of a substance which promotes the solubility upon which the gelatinization depends. Such substances are the acetic ethers of glycerine, ethyl, methyl, acetic acid, a mixture of alcohol and ether, acetone, nitro-benzol, dinitro-benzol, the nitrates of methyl, ethyl, and other analogous substances. The quantity of the solvent which has to be added depends upon the nature of the substance chosen; but, as a rule, about 10 per cent. of the weight of the nitro-glycerine which has to be gelatinized will be found in practice to be amply sufficient. Moreover, by gently heating nitro-glycerine (in a water bath or otherwise), it acquires the property of dissolving nitrated collodion cellulose without the addition of the promoting solvent, as above described. That property admits of dispensing entirely with the addition of the promoting solvent; or when it is found advantageous to use the promoting solvent, the application of heat will enable the quantity used to be reduced to 2 per cent., or even less, of the weight of the nitro-glycerine. Since nitrated cellulose is rarely, if at all, of a homogeneous composition, and therefore its solubility in nitro-glycerine will be found to vary, the necessity for adding a promoting solvent must be ascertained by experiment.

The above-described process of gelatinization necessitates (1) that the explosive liquid shall contain no impurity or foreign matter capable of counteracting its power of dissolving nitrated cellulose, or other substance possessed of the same property, as hereinbefore described; (2) that only such nitrated cellulose or other analogous substance is to be used which readily dissolves in and gelatinizes the explosive liquid; (3) that the solution of the nitrated cellulose or other analogous substance (especially if that substance is twisted or compressed) shall be facilitated by mechanical stirring or kneading, so as to allow of the necessary access to all the parts of the nitrated cotton intended to be dissolved.

The explosive jelly obtained by the above-described process can be easily pressed into cartridges, or any other forms convenient for use. For certain purposes, and especially for military use, it is of importance to be able to dilute or modify the explosive sensitiveness of gelatinized nitro-glycerine in a measure exactly suited to the purpose in view. This is done by adding more or less of a non-explosive or sluggishly-explosive substance, possessed of the property of dissolving both nitro-glycerine and the substance which serves to gelatinize it. Such are the acetic ethers of glycerine, methyl, ethyl, and acetone, acetic acid, nitro-benzol, dinitro-benzol, the nitrates of methyl and ethyl, or other solvents of an analogous character. An addition of the

above-named, or of any analogous substance, serves not only the purpose of rendering the gelatinized nitro-glycerine less sensitive to concussion, but also reduces its quickness of explosion, facilitates, as above described, the process of gelatinization, and lowers the temperature at which nitro-glycerine becomes hardened or congealed. The least volatile substances, such as the acetic ethers of glycerine, nitro-benzol, dinitro-benzol, deserve preference, inasmuch as they cannot become inactive through evaporation.

Gelatinized nitro-glycerine, when properly confined, can be exploded by a common fuse; but, as a rule, detonators, containing a strong charge of fulminate, are used, and also for firing dynamite. When hardened in cold weather, gelatinized nitro-glycerine explodes more readily than frozen dynamite; still it is a good precaution always to head the charge with a primer, consisting of a small cartridge of gunpowder or gun-cotton, or dynamite, or uncongealed gelatinized nitro-glycerine, or analogous substance.

The great success of dynamite has given rise to numerous other nitro-glycerine compounds, of which the most known are lithofracteur, the ammonia, Colonia, and Hercules powders, Horsley's powder, dualine, seranine, and dynamite No. 2.

Colonia and *Hercules powders* are mealed gunpowder mixed with nitro-glycerine, resembling the first nitro-glycerine preparation brought out in 1863.

Seranine and *Horsley's powder* are chlorate of potash preparations mixed with nitro-glycerine. The substitution of a chlorate for a nitrate is said not to add to the power, while it adds to the expense of the compound, and also somewhat increases its danger.

Dualine was brought out by DITTMAR in Germany. It consists of sawdust, nitrate of potash, and nitro-glycerine.

Lithofracteur.—The ingredients as now published by the manufacturers are:—Nitro-glycerine, 55 per cent.; kieselguhr, 21 per cent.; charcoal, 6 per cent.; barium nitrate and bicarbonate of soda, or either of them, 15 per cent.; sulphur and manganese oxide, or either of them, 3 per cent.

The first description of "lithofracteur," as given by the inventor, J. A. FROITZHEIM, in his patent specification of 1872, was a very extraordinary one. After stating that he substitutes the "small scales of fresh water fish mixed with carbonate of soda and nitrate of potash" for kieselguhr, the patentee continues:—"Nitrate of baryta, manganese, double carbonate of soda, and prepared sawdust are mixed in a solution of resin and spirits of wine in about the following proportions—70 parts nitrate, and the rest of the above-named materials. This mixture is mixed in a damp state with the prepared infusorial earth. After this second mixture is carefully prepared, a third mixture is made by sprinkling that already obtained with a solution of sulphur or bicarbonate of sulphur, and then by adding finely ground burnt bones or coal.

"This mixture is then further manipulated in other rooms as follows:—Firstly, it is mixed with bran and prepared sawdust, which are saturated with nitro-glycerine; this is repeated most carefully with the hand until the requisite quantity of nitro-glycerine is absorbed. This explosive is then formed into cartridges of any required size in separate rooms, and then carefully packed. The quantity of nitro-glycerine which is requisite for the perfecting of good 'lithofracteur' is from 45 to 50 or 55 per cent.; but I do not bind myself to this quantity, as the amount of the nitro-glycerine will depend upon the nature and tenacity of the material to be blasted.

"The following example is sufficient to explain the proportional parts of the ingredients used, and the method of manufacturing 'lithofracteur' or 'Krebs' explosive,' but I reserve to myself the right to vary those proportions, also the suppression of any one or more of the ingredients in the manufacture of explosives, as circumstances may dictate:—20 parts of a mixture composed of 70 parts of ground nitrate of baryta, 10 parts manganese, 10 parts bicarbonate of soda, and 9 parts prepared sawdust, with a solution of 1 part resin in 5 parts spirit. This mixture is mixed with a second composition prepared of silica. To prepare the same, 100 parts thereof are mixed with 2½ parts carbonate of soda, and 2½ parts nitrate of baryta, which after being mixed is heated dry, ground, and sifted if required. 17½ parts after the above have been thoroughly mixed make a preparation of 7 parts of sulphur dissolved in bisulphuret of carbon, which contains 2 parts solution of sulphur added to 3 parts finely ground and sifted charcoal. To this mixture are then added 1 part prepared sawdust, and 1 part bran previously saturated with nitro-glycerine, adding the rest of the nitro-glycerine in small quantities to the whole composition, until 55½ parts nitro-glycerine have been added."

Some time ago the dynamite and lithofracteur of Messrs. KREBS & Co., of Cologne, were analyzed by ULEX, sworn chemist in Hamburg. The dynamite contained 66 per cent. of nitro-glycerine, 6¼ per cent. nitrate of barium, and 27 per cent. of infusorial earth. The lithofracteur contained 70 per cent of nitro-glycerine, 5 per cent. of nitrate of barium, 2 per cent. of coal-dust, and 23 per cent. of infusorial earth.

Ammonia powder, invented by OHLSON and NORRBIN, though comparatively unknown, is far stronger than lithofracteur, and surpasses even dynamite in point of power. Its only drawback is the hygroscopic nature of its chief ingredient, which is ammonium nitrate. But in every other respect it is a very superior blasting agent. It consists of 80 parts by weight of nitrate of ammonium, 6 parts of charcoal, and 14 to 20 of nitro-glycerine.

Dynamite. No. 2 contains substantially the ingredients of gunpowder, less sulphur, *plus* nitro-glycerine, and is used for blasting soft rocks.

Sebastin, patented by G. FAHNEJELNS of Stockholm, contains charcoal as the absorbing material.

In order to produce a charcoal having the required qualities, the carbonization or coking must be done in such a manner as to completely destroy the organic

substances, and to produce as porous a charcoal as possible. For this purpose young trees or striplings, or branches of poplar, hazelwood, or alder tree are selected and burned in an open fire.

When the wood has been consumed the fire is not put out by means of water, but left to go out of itself. In this way a very inflammable and very porous charcoal is obtained, which can absorb more than five and approaching to six times its weight of nitro-glycerine. The charcoal is pulverized in a wooden mortar; but should not be reduced to too fine a powder, else it will not so completely absorb the nitro-glycerine.

The charcoal produced in the ordinary way is quite different as regards absorbing power. Charcoal of fir tree may, however, be used, if charred a second time in a special oven.

By mixing different kinds of charcoal a material may be obtained possessing the required absorbing qualities, and an explosive compound may then be obtained of the required power without loss of the necessary consistency; that is, without being too dry, which is not desirable. The charcoal not only serves as a good absorbent for the nitro-glycerine, but it plays also an important part in the combustion. The nitro-glycerine in exploding decomposes into steam, carbonic acid, nitrogen, and oxygen. In the explosion of dynamite with inert base, the oxygen goes away without being utilized; but in the explosion of this new compound a part of the absorbent charcoal is burnt by means of the liberated oxygen; the quantity of gas is thus augmented, and also the development of heat, whereby again the tension of the gas is augmented. As, however, the quantity of charcoal necessary for the complete absorption of the nitro-glycerine is in all cases much larger than that which can reduce the excess of oxygen produced at the explosion, nitrate of potash is added.

Brain's powder contains chlorate, in the place of nitrate of potash; and as absorbent, coal-dust, or sugar, or starch, or any carbonaceous material.

The Rhenish Dynamite Company manufacture a dynamite which is composed of 70 parts of a solution of 2 to 3 per cent. of naphthaline in nitro-glycerine, 3 parts of chalk, 7 parts of heavy spar, and 20 parts of purified infusorial earth.

The most vital question which concerns explosives is the evolution, or rather concentration, of their power, absolute and relative. This is a subject to which serious attention has long been given, without leading as yet to a satisfactory result.

It is not only from a theoretical point of view that such knowledge is of importance. The manufacturers of explosives are frequently themselves unable to estimate the relative value of other powders and their own.

The Government commission appointed in 1864, to report on the application of gun-cotton to mining and quarrying operations, also "became strongly impressed with the great difficulty of instituting really comparative blasting and quarrying operations. In rock which appears uniform and quite sound, the blasting often brings to light veins, shakes, or fissures, which render a comparison of work done in two contiguous portions impossible.

Explosive power may be estimated in two ways, viz., indirectly by theoretical induction, and directly by measuring the maximal tension of the gas at the moment of the explosion, or the mechanical work which it is capable of performing. For gunpowder both methods have been applied without showing much discrepancy in the final result. Captain NOBLE and Professor ABEL'S recent experiments show that the maximal pressure exercised by gunpowder, when the density of the products of the explosion is equal to 100, or, in other words, when 1 kilo. of exploded powder occupies the volume of 1 litre, is equal to 6400 atmospheres, or about 42 tons per square inch; that its explosion produces about 705 units of heat, which, multiplied by its mechanical equivalent, represent a theoretic work of 486 foot-tons per pound of powder.

But highly satisfactory as are those figures, derived from actual measurements, they give no clue to find the absolute or relative power of gun-cotton, nitro-glycerine, and other violent fulminates of modern application. These have been considered too powerful and too quick of explosion for even the strongest steel receptacle to resist their action, and hence, as far as we know, no attempt has hitherto been made to measure their explosive pressure by an instrument similar to those employed by Captain NOBLE and others to estimate the tension produced by exploding gunpowder.

By aid of repeated calorimetric tests made at the Depôt Central des Poudres, Paris, ROUX and SARRAU have sought to determine how much heat the explosion, or rather detonation, of various fulminates produces. They have thus found for nitro-glycerine 1784, for gun-cotton 1123, and for picrate of potash 840 units of heat, which, multiplied by the mechanical equi-value per unit, gives 778, 489, and 366 métre-tons per kilo. of the substance, as against 378 for the best sporting powder, and 267 for the ordinary trench-mining powder, which is of a very inferior quality. Comparing those figures with the heat produced by the combustion of gunpowder, as found by ABEL (704 units), and taking it as 1·00, the mechanical power which nitro-glycerine is capable of performing would rank as 2·53, that of gun-cotton as 1·59, and picrate of potash 1·19.

BERTHELOT, following a different method, purely theoretical, arrives at much lower figures for the heat produced by the combustion of the same substances, and consequently also for the amount of work it represents. He admits that at the very high temperature which is a very general feature of explosive combustion, no complex chemical combination can exist, and that only elementary compounds, such as water vapour, carbonic oxide, and carbonic acid will be formed; so that when the chemical composition of such explosive substances is known, which are entirely converted into gas, it is easy to determine, without recourse to experi-

ments, the nature of the gaseous products formed at the moment of their explosion. Hence, for instance, nitrate of ammonium, of which the formula is $NH_4.NO_3$, would split up into $N_2 + O_2 + (H_2O)_2$.

Starting from this point of view, the correctness of which certainly does not appear to admit of the slightest doubt, BERTHELOT computes, from well known tables, the heat produced by the formation of the gaseous products from their elements. He further evacuates the units of caloric developed in the formation of the explosive substance to be dealt with from its elements, and takes it for granted, of course, that as much heat must be absorbed in disuniting the chemical tie as was freed in forming it. The heat lost in that operation he deducts from the sum of heat produced by the reunion of the disconnected elements, the balance representing the heat really developed in the explosive combustion. Thus, for each 227 grams. of nitro-glycerine, which the explosion transforms entirely into carbonic acid, water, nitrogen, and oxygen, BERTHELOT calculates the heat produced by the formation of the carbonic acid and water from the elements at 430,500 units, and the heat produced by the formation of the nitro-glycerine itself from its prime elements at 130,500 units, which, deducted from the total of 430,500, leaves 300,000 units of caloric freed, or 1320 units per gram. of nitro-glycerine exploded.

NOBEL has for the last six years made regular use of a method based on measurement of the ballistic power of explosives; and though certainly open to some objections, it has the advantage of being extremely handy and sufficiently accurate for the object in view.

A mortar test is indeed more reliable for comparing detonating explosions than for slower compounds; for, in the latter case, the projectile may have left the mortar before the combustion is completed, while, in the case of fulminates, their explosive conversion is so rapid that in all probability it is completed before the projectile has begun to move at all, thus acting upon it with the whole force of its initial tension. This is further confirmed by the fact that the bore of the mortar can be made far shorter than for testing gunpowder, without any considerable falling off of the range of projection.

The table here annexed shows the results obtained in testing the ballistic power of detonating gun-cotton, nitro-glycerine, dynamite, and various other compounds. From the figures therein contained some important conclusions may be drawn.

No. of Experiments.		Parts by weight.	Weight of charge in grams.	Distance thrown (shot = 32 lbs. weight) in links.			Average in links.
				1st charge.	2nd charge.	3rd charge.	
1	Nitro-glycerine, pure,	—	5	308	297	295	300
2	Nitro-glycerine,	3					
	Compressed gun-cotton,	3	6	290	302	305	299
3	Potassium chlorate,	122					
	Charcoal,	20	7	250	241	243	245
	Nitro-glycerine,	30					
4	Potassium nitrate,	101					
	Charcoal,	17	10	279	263	281	274
	Nitro-glycerine,	25					
5	Ammonium nitrate,	80					
	Charcoal,	6·5	6	299	300	302	300
	Nitro-glycerine,	20					
6	Gun-cotton compressed,	—	7	295	315	290	300
7	Patent gun-cotton powder,	—	8	291	305	288	294
8	Fulminate of mercury,	—	10	185	—	—	185
9	Fulminate of mercury,	80	10	220	219	219	219
	Chlorate of potassium,	20					
10	Gunpowder mealed,	80	10	305	298	295	299
	Nitro-glycerine,	20					
11	Curtis and Harvey's extra strong blasting powder exploded with detonator,	—	20	341	340	330	337
12	Picrate of potassium,	60					
	Nitrate do.	30	7	222	237	229	229
	Nitro-glycerine,	10					
13	Sodium nitrate,	85					
	Charcoal,	17					
	Sulphur,	16	10	282	307	313	301
	Nitro-glycerine,	30					
14	Lithofracteur * as per government license :—						
	Charcoal,	6					
	Kieselguhr,	21					
	Barium nitrate,	15	7	218	211	205	211
	Sulphur,	3					
	Nitro-glycerine,	55					
15	Dynamite No. 1, consisting of :—						
	Nitro-glycerine,	75	7	290	318	307	304
	Kieselguhr,	25					

* This is the strongest mixture of lithofracteur ingredients as published by the manufacturers. The slightest addition of sodium bicarbonate or manganese dioxide indicates a decrease of power, as shown by numerous mortar tests.

If the ballistic power of detonating nitro-glycerine is expressed by 100, then in their comparison, weight for weight, compressed gun-cotton ranks as 71; dynamite, consisting of 28 per cent. of guhr and 75 per

cent. of nitro-glycerine, as 72; ammonia powder, as 83; gunpowder mixed with 20 per cent. of nitro-glycerine, as 50; gun-cotton mixed with its own weight of nitro-glycerine, as 83; Curtis and Harvey's strongest blasting powder, ignited with a detonator-cap, as 28; fulminate of mercury, as 30; and lithofracteur of the strongest kind (made of the ingredients as specified in the Government licenses for that material), as 50·5.

In this estimate no deduction has been made for the power exercised by the fulminate of the detonator-caps, it being the same for all preparations, except gun-cotton, for which 0·16 additional weight of fulminate was used.

Interesting as it may be to compare the relative power of explosive substances, weight for weight, the power which they are capable of exercising, bulk for bulk, is of far greater importance in their application to blasting. It is easily computed when their specific gravity is known, which has been found for nitro-glycerine, 1·6; for gun-cotton, 1·00; for dynamite No. 1, 1·65; for ammonia powder, 1·55; for gunpowder, 1·00; and for lithofracteur, 1·20, which is also the specific weight of dynamite No. 2, and of most nitro-glycerine preparations containing large quantities of metallic salts.

When their power is compared, bulk for bulk, the various explosives range as follows:—

Nitro-glycerine,	100
Ammonia powder,	80
Dynamite No. 1,	74
Lithofracteur,	53
Gun-cotton,	45
Curtis and Harvey's blasting powder fired by detonator,	17·5

Blasting.—There should be no air-chamber round the charge, for the expansion which it causes not only lessens the power in proportion to its dilution, but actually decreases the tension of the gas in a much greater measure. In the case of blasting powder such air space cannot be avoided, in consequence of its influence on the quickness of combustion. But with nitro-glycerine it seems as if its liquid state would specially favour the exclusion of all empty space, and so it does when it can be poured direct into a blast-chamber. But apart from the impossibility of pouring a liquid into horizontal bore-holes, or such as incline upwards, experience has shown that there is very great danger connected with that practice under any circumstances. An almost imperceptible seam or fissure in the rock —and they scarcely ever fail—will cause a part or the whole of the liquid charge to leak into the smallest cavities, and remain there until the miner, in drilling a new bore-hole, strikes it, or strikes the rock in its proximity, when it goes off, causing a fearful accident. Hence nitro-glycerine cannot be safely used without cartridges. These, to hold a liquid, must be strong, which makes them rigid. They cannot be introduced into a bore-hole without leaving a considerable air-chamber round the charge, particularly as bore-holes generally deviate a great deal from the circular shape. It is difficult to calculate even approximately the relative proportions of the unoccupied space and the charge, but certainly with such small size diameter of bore-holes as are generally adopted for blasting with nitro-glycerine, the loss is at least equal to one-third of the whole space, so that 3 cubic inches of the chamber will hold on an average only 2 cubic inches of the explosive liquid. Dynamite has here all the advantages on its side, and it is very much to be regretted that miners very frequently neglect to make use of it. Being highly plastic, the slightest pressure with a wooden rod compresses the charge in the bore-hole, so as to exclude all empty space. It is true that the small primer cartridge cannot be treated in the same manner, lest the detonator-cap affixed to it should be dislodged. But it forms only the upper part, and a very small portion of the charge, and the air-chamber which surrounds it is therefore of no practical importance. The increased effect derived from this mode of applying plastic explosives is far greater than is generally believed. All nitro-glycerine preparations possess the same advantage, but none are quite as plastic as dynamite. Nearest to it is lithofracteur. Gun-cotton, like nitro-glycerine, leaves a considerable air-chamber, owing to its rigidity, as made into cartridges.

Practically the advantage of being able to fill up the blast-chamber in a bore-hole amounts to the same as if the specific gravity of the same explosive could be increased so much as to make up by weight for the want of bulk. In other words, what has to be considered is not the specific gravity of the explosive itself, but of its gaseous products at their moment of initial tension, when they strike the rock or other resisting medium.

Since nitro-glycerine cannot with any degree of safety be used without cartridges, and since the unavoidable air chamber represents an average of one-fourth, at the very lowest estimate, of the blast chamber, a proportionate reduction should be made in computing its useful effect for blasting purposes. Dynamite thus rises nearly to its level, and ammonia powder becomes somewhat superior.

From the mortar experiments already referred to an approximate estimation may be formed, not only of the power of nitro-glycerine preparations containing an explosive base or absorbent, but also of the power whereby that explosive contributes itself, and when it detonates under the influence of detonating nitro-glycerine. For that purpose it suffices to make out the quantity of nitro-glycerine contained in a compound, and compute the distance of projection to which it would carry the projectile of the testing mortar. The balance of projections is due to the other ingredients, and permits of a tolerably near elevation of their relative power. It is true that the gaseous products of the exploded nitro-glycerine and those of its explosive partner may react on each other, and cause a slight loss or gain of power, but it cannot materially alter the relative value of the two.

The result of such a calculation shows that weight for weight, when nitro-glycerine figures as 100, chlorate of potassium powders rank as 29 to 30,

nitrate of potassium powders as 20 to 22, and nitrate of sodium powders as 22 to 23.

Under certain conditions otherwise similar a quick explosion is preferable to a slow one for blasting. The same amount of expansion is produced in either case, but the maximal tension of the gas developed may be vastly different, and on that tension depends the blasting power. For instance, mealed gunpowder under certain conditions burns with a tension scarcely sufficient to burst a straw, yet the same substance becomes under other conditions capable of tearing the hardest rock. The difference in action is due only to a difference in the rapidity of combustion.

It is therefore clear that of two explosives the more powerful one may, for want of quickness of combustion, be the less efficacious for blasting, and it becomes a matter of considerable importance to possess a ready means of overcoming the drawback of the slow action. This difficulty has been overcome by adopting a special mode of firing explosions, known as the detonating ignition. It consists in applying a strong local explosion instead of a spark or flame, and it modifies in a remarkable degree the natural quickness of combustion exhibited by explosive substances.

It is especially in connection with nitro-glycerine that this mode of ignition has led to remarkable results, and it was to suit the peculiar nature of that substance that it was invented. Nitro-glycerine indeed, without that special firing, though it is an explosive, is no blasting agent, as it cannot be applied with any degree of certainty that it will go off. Not so when fired by a local explosive. It not only detonates without any confinement, but it affords an extraordinary facility for setting off substances which without its aid are absolutely inexplosive. If, for instance, charcoal and nitrate of potassium are mixed without sulphur, they form no explosive compound within the ordinary meaning of that term; but if from 10 to 15 per cent. of nitro-glycerine are added, a local explosion, produced by a strong detonator or fulminate cap, will cause the almost inert mixture to detonate with nearly the same rapidity as the n tro-glycerine itself. Nitrate of ammonium and charcoal, with or without sulphur, form a mixture so sluggish at the ordinary temperature, that when tried in a shell along with 6 ozs. of gunpowder, the explosion of the latter failed to set it off, or even to inflame it; yet mixed with 15 per cent. of nitro-glycerine, it detonates with an extraordinary violence. Sawdust, bark, rosin, starch, sugar, glucose, flour, dextrine, gum, &c., mixed with any nitrate, become, if a small portion of nitro-glycerine is added, most violent detonating fulminates. Nor is that all. Substances considered as absolutely incombustible will form explosives. For instance, chloride of ammonium, mixed with nitrate of potash and nitro-glycerine, will decompose explosively under formation of chloride of potassium, and the freed hydrogen unites with oxygen of the nitrate. Sulphates are very much more sluggish; but if very finely divided and mixed with charcoal, they also indicate a decided reaction, although too slow to be completed in the extremely short time which an explosion occupies. Chlorate of potash mixed with nitro-glycerine detonates even without the presence of charcoal or any other combustible. The number of organic compounds, soluble or even insoluble in nitro-glycerine, which can thus be brought to detonate is almost unlimited.

This extraordinary influence which the presence of nitro-glycerine exercises on slow explosives, and even seemingly inert substances, is easily accounted for. Being a liquid, it comes in very close contact with the mixtures, and when the detonation ensues the fine layer of nitro-glycerine which adheres to every grain is instantaneously converted into an extremely dense atmosphere of gas, having a temperature of at least 3000° to 4000° C. Such a bath must quicken even the slowest combustion.

It is exactly the same cause which makes gunpowder burn with extreme quickness in a gun, while its combustion in the open air is comparatively slow. When confined the hot gas accumulates in proportion as it is being generated, and the denser it grows the more heat it brings to bear on the reaction, which thus becomes almost instantaneous.

The action of the detonator-cap in setting off nitro-glycerine and other explosives is far more complicated, and not so easily explained. Some attribute it only to the heat produced by compression, some only to the heat of the gas given off by the fulminate of the cap, and others, again, to the dissociating power of a strong vibration. It is not unlikely, at least in some instances, that all those influences are brought to bear on the explosion, but it would be very difficult, indeed, to compute the part contributed by each. There can be no doubt as to the dislocation of certain unstable compounds by vibration alone, since the slight shock which sets off chloride and iodide of nitrogen, perchlorate of ethyl, &c., cannot possibly raise their temperature, even locally, to the degree at which they explode. Even in the case of nitro-glycerine, which exhibits no such extreme sensitiveness, direct experiments have shown that very violent vibration can cause it to explode. But if vibration alone suffices to set off nitro-glycerine, it is still less doubtful that heat alone will do it. Not only does it detonate by being raised to the temperature at which its constituent elements dissociate, but a minute charge of gunpowder, so slightly confined that the gas which it produces has a very feeble tension, never fails to make it detonate. It suffices, indeed, to apply heat in any shape, so that it acts upon a very large surface of nitro-glycerine, for then the gas evolved can no longer escape as quickly as it is produced, and the pressure, accumulating with immense rapidity, brings on the explosion.

Nitro-glycerine preparations and gun-cotton cannot be brought to detonate by such means, but go off easily under the influence of a sharp local explosion, such as produced by a fulminate. Two opposite tendencies are here at work, with one to set off the explosive acting on it by heat, vibration,

or whatever cause it may be, and the other to throw it away by the propelling impulse due to the expanding gas. Both must be extremely quick in operating, and it is therefore easy to see how a slight, apparently insignificant, difference may turn the scale and cause an explosion or a miss-fire. For instance, in grinding chlorate of potassium and sulphur with care in a mortar, a series of small detonations take place, which do not spread, but a somewhat stronger blow or friction will set off the whole. Evidently in one case the propelling power is preponderant over the igniting tendency, in the other it is not. Even the quickest substance requires time to get heated, and unless the velocity implanted allows that time combustion cannot take place.

Professor Abel found by repeated experiments that a charge of fulminate amply sufficient to set off compressed gun-cotton failed to explode the same material in a loose form; but by twisting loose, uncompressed gun-cotton round the cap, and securing it well with a string, so as to increase its density and resistance to projection, it is brought to detonate with great facility without increased charge of fulminate. It has also been found that loose gun-cotton detonates more readily if impregnated with quite inert substances than in its isolated state, evidently because the additional weight opposes additional resistance to motion, thus allowing time.

The reasoning which led to firing slow explosives by local detonation was this:—When a hammer strikes a very thin layer of nitro-glycerine on an anvil the blow produces a strong compression of the liquid, which liberates heat, and raises its temperature to the point at which it detonates. But only that part which actually receives the blow explodes. If, however, the hammer is very heavy, and the blow strong, the explosion is not confined to the part which receives the direct shock, and the whole goes off. A local detonation, owing to the immense tension of its gas, must be very similar in action to a strong blow, and will thus compress the explosive liquid which surrounds it, causing it to detonate at will, and to propagate the explosion throughout the whole mass by the same means.

The dangers arising from the use of explosives are due to four causes, viz., the contact with fire or heated surfaces, concussion or percussion, want of chemical stability, and the poisonous character of the fumes produced by their explosion.

Danger from fire in connection with gunpowder has been illustrated by so many accidents of more or less magnitude, even recently, that a comparative immunity from that danger cannot be too much welcomed in a new power. Modern explosives offer that immunity to a remarkable degree, which is the more valuable since it in no way interferes with their quickness of explosion when called for. Both gun-cotton and dynamite have been burned over fire in large quantities, as much as 1 cwt. or more at a time, without giving rise to the slightest explosion or loud report. Such a behaviour certainly is a great safeguard against accidental firing, but it is very apt to produce over confidence, and lead uneducated people to mistake relative for absolute safety.

What is needed for the safety of a blasting powder is not that one should be able to fire it in large quantities with impunity, but only that it should not be fired by a spark; and if accidentally fired by a flame, should allow reasonable chances for escape. In that respect both dry compressed gun-cotton and ordinary dynamite possess many advantages over gunpowder; and as for wet gun-cotton and some kinds of dynamite, for instance ammonia powder, they are absolutely more difficult to get to burn than most inert combustibles are. A gun-cotton factory might be burned down, all but the drying-house, where the quantities may be very small at a time, without danger of an explosion. A nitro-glycerine factory is practically almost as safe with regard to mere firing, for the liquid explosive is kept confined in receptacles wherein no fire can come at it, and besides, a mere spark does not set it off. Dynamite is slow to catch fire, but burns rather fiercely when fired, and if the quantities are large or under confinement an explosion may finally ensue; but it cannot be ignited by a spark, and if fired by a flame it leaves time to the workers to save themselves before an explosion sets in.

There is a kind of danger special to nitro-glycerine preparations, against which miners cannot be too much or too frequently warned. Owing to the property of the nitro-glycerine contained therein crystallizing at a low temperature, it becomes hardened, and must be frequently thawed in winter to refit the cartridge for use. In spite of warning instructions contained in every 5 lb. package of dynamite, and of very suitable warming pans, wherein the operation is easily and safely performed, miners will insist on doing it in their own way; and it is almost impossible to make them understand how a cartridge, which firing does not set off, cannot be slowly heated with the same impunity. Thus they will roast nitro-glycerine preparations near a fire or on hot cinders, or wherever there is real danger to put them, and only too frequently accidents are due to that cause.

Danger from concussion, which has proved so disastrous with nitro-glycerine, has never, as far as known, been the cause of any accident either from gun-cotton or dynamite. But this immunity is only in a very small degree due to the cause to which it is almost universally ascribed. There is a notion abroad that dynamite is quite insensible to a blow; that the porous material called kieselguhr cushions the nitro-glycerine particles so as to change completely the explosive properties; that the liquid explosive, when absorbed in porous silica, becomes endowed with much greater chemical stability. For this opinion there is scarcely any foundation. The main danger to nitro-glycerine arose from the sensitiveness to concussion which it acquires through contact with a hard metallic, strongly vibrating substance, such as the tin canisters in which it was contained. The main safety of dynamite is derived from the absence of any hard vibrating material in

immediate contact with the nitro-glycerine which it contains.

A tin cartridge filled with nitro-glycerine is not exploded if it drops from a height of several hundred feet on to soft ground; yet that same tin cartridge, falling only 3 feet high on an anvil, bottom foremost, is sure to set the charge off, though there is not a particle of the explosive on the outside.

I tshould be borne in mind that water has the property of displacing the nitro-glycerine in dynamite; the cartridges must therefore be kept dry, and the packing made water-tight as far as practicable.

Gun-cotton requires no such precautions, and ranks, as regards safety from concussion in manufacture and transit, first amongst modern explosives. However, the danger most dreaded in modern explosives is not from concussion, but from their liability to chemical decomposition, productive of heat, which sometimes leads to ignition and explosion. This is a matter of weighty consideration, and those who carry or store explosive substances are fairly entitled to require that they should not go off without external cause.

It is only recently that the true cause of chemical instability, which belongs to the whole class of nitrated organic compounds, has been clearly defined.

After their nitration a certain portion of acid, sulphuric, nitric, and hypo-nitric, always adheres to those compounds, more or less, according to their form and structure. From a liquid explosive substance the acids are easily washed out, by churning it with water first and then with alkaline solution. But a granular, flocky, or fibrous material retains the acids with far greater tenacity, particularly the nitrous and hypo-nitric acids, which every nitrated organic compound has a strong tendency to retain.

It is quite clear that if there is hypo-nitric acid present, that highly corrosive material, which attacks almost every organic compound, even at the ordinary temperature, must be removed; if not it will slowly, but surely, lead to an incipient decomposition, which, acting on a nitrated substance, sets free portions of dioxide of nitrogen or hypo-nitric acid.

From nitro-glycerine the corrosive acid is washed out with the utmost facility, and from the moment when the importance of that operation became fully appreciated it has never been neglected. Hence the chemical stability exhibited by dynamite under all conditions of climate. It sometimes indicates an acid reaction; but that is due to the absorbent, and not to the slightest trace of hypo-nitric acid present.

The great influence of even the minutest quantity of hypo-nitric acid in starting a decomposition is not very easy to demonstrate by actual experiments on gun-cotton, or any analogous substance; but it is rendered very plausible by mixing together certain substances, such as spirits of wine, or glycerine and nitric acid, with or without addition of nitrate of urea, which frees it from hypo-nitric acid. The pure nitric acid produces no decomposition even at a high temperature, while the slightest quantity of hypo-nitric acid will bring about, more or less quickly, even at 0° Centigrade, a violent decomposition. A similar use of nitrate of urea for neutralizing hypo-nitric acid in dried gun-cotton would not have the same effect, for alkali or amide must be in solution, so that atom touches atom; if not, the reaction is localized, and cannot be depended on.

Dr. Sprengel has started the ingenious idea of adding for the same purpose a soluble organic base to nitro-glycerine, but when the nitro-glycerine crystallized it would separate from the base, and on being thawed a uniform solvency might not readily take place.

Undoubtedly the chemical stability of organic nitrated compounds is to a certain degree imperfect, and it is very desirable that they should be so far improved as to stand for any length of time exposure to the temperature of boiling water. This is not as yet the case with either gun-cotton or nitro-glycerine, even when both are thoroughly washed.

Although nitro-glycerine has exhibited upon the whole greater chemical stability than gun-cotton, yet it acquires that superiority only after being thoroughly purified from acid at the factory. When it contains free hypo-nitric acid it cannot be stored at all in hot weather, and even during the course of its manufacture it has several times given rise to a decomposition, ending with explosion and loss of lives. The instability of the crude article contrasts so strongly with the stability of the pure nitro-glycerine in dynamite, as to remove every trace of doubt regarding the decomposing influences of the adhering acids.

Local accidents from modern explosives are almost exclusively to be attributed to injudicious thawing of nitro-glycerine preparations, to reckless removal of the tamping in bore-holes after a miss-fire, to forcing in gun-cotton cartridges too wide for the bore-hole to receive them, and to playing with the detonator-caps.

Amongst the most grievous complaints of miners about modern explosives is the poisonous nature of the fumes emitted, which exposes them to most serious inconvenience.

Slight attention was paid at the beginning to those complaints, partly because if fumes are injurious miners must allow them time to draw off, or the proprietor must increase ventilation; partly also because it is almost impossible to accord the notions of modern chemistry with the existence of poisonous fumes. The great power of a detonating substance, like gun-cotton or nitro-glycerine, can only be explained by the high temperature of the gaseous products produced, and theory tells and practice proves that at very high temperatures no complex chemical combinations can exist. Hence nitro-glycerine, when it detonates, must split up into carbonic acid, carbonic oxide, water, and nitrogen. Under such circumstances it seemed difficult to explain the reiterated complaints of poisonous fumes coming from the mines. About their

existence there can no longer be any doubt, and the poisonous element consists of hypo-nitric acid, against which ammonia would prove a very effective remedy. But such fumes are never the products of a rational use of the explosive substance, and it is quite evident that hypo-nitric acid can never escape decomposition in an atmosphere of 3000° C. or more with combustible elements in presence.

It does not. But when a dynamite cartridge burns instead of exploding, the combustion takes place at a much lower temperature, and the nitric acid contained in the nitro-glycerine gives off only part of its oxygen, forming dioxide of nitrogen, which escapes, and in contact with the atmosphere gets converted into hypo-nitric fumes. It is easy to become convinced by actual experiment of the different atmosphere produced by a cartridge when burning or exploding. In the worst ventilated tunnel twenty cartridges may be detonated without as much molestation as is caused by the burning of one.

The frequent occurrence of bad fumes in mines proceeds from the general mistake of not securing the detonator-cap to the fuse, and the fuse to the cartridge. In charging, the miner under such circumstances easily draws fuse and cap out of the cartridge, leaving them separated, so that the cap cannot possibly exercise its detonating influence. What then takes place is this. Part of the dynamite burns, emitting hypo-nitric fumes, and part generally explodes under the influence of accumulating heat and pressure. Thus the charge goes off, but with a far inferior effect to that of a proper detonation, and with emission of a great deal of red fumes of hypo-nitric acid.

The poisonous character of nitro-glycerine has been referred to above. Should in some cases the death of a person be suspected to be due to this substance, the following method will serve to give evidence for the existence of nitro-glycerine in the body. Parts of the body, liver, intestines, &c., are extracted with ether or chloroform; a few drops of the extract are placed in a watch-glass, mixed with two or three drops of aniline, evaporated until ether (or chloroform) and water have gone off, and to the residue a drop of concentrated sulphuric acid is added. If nitro-glycerine is present the contents of the watch-glass will assume a crimson colour, due to the reaction between aniline sulphate and nitric acid, the latter having been liberated from the nitro-glycerine.

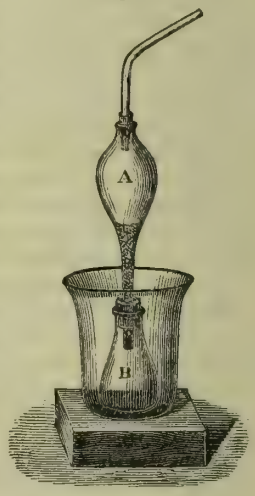
OIL.—*Huile*, French; *Oel*, German; *Oleum*, Latin. —Oily bodies are generally divided into two classes, fixed or fat oils, and essential or volatile oils. The two are, however, entirely dissimilar, both in properties and composition; indeed, except in the one common property of greasiness, they are not at all allied to each other. The essential oils emit at ordinary temperatures a distinctive, odorous, and penetrating vapour, and when dropped on paper do not produce a permanent greasy spot; while the stain of a fixed fatty oil does not disappear by exposure, nor even when the paper is subjected to a gentle heat.

Fats and fixed oils contain a very large proportion of carbon, as compared with that of the other constituents — a character that distinguishes this class of substances from the greater number of compounds of organic origin. In many instances the amount of carbon is from 70 to 80 per cent., and upon this property depends their great value as food, and as sources of light.

SOURCES.—Oils are found abundantly in the vegetable and animal kingdoms. They occur in various parts of plants, but principally in the cellular structure of seeds, and in the fleshy pulp which surrounds them. That part of the seed which gives birth to the cotyledon contains most. The seeds richest in oil are those belonging to the genus *Cruciferæ*, and next to that are the *Drupaceæ*, *Aomentaceæ*, and *Solaneæ*. Linseed contains 20 per cent. of oil, rape from 35 to 40, castor seed 60 per cent., and nuts about half their weight. The quantity of oil furnished by seeds varies, not only with the species, but in the same seed, with climate and method of cultivation. The seeds should be ripe, fresh, and of good quality. The yield of oil is always less than that actually contained in the seed, and the quantity remaining in the *marc* or pressed cake is greater in proportion as the starchy, ligneous, and albuminous principles predominate.

Estimation of Oil Seeds.—The exact quantity of oil contained in seeds is estimated by taking a given quantity of seed, bruising it, and treating it repeatedly with ether, until the oil is completely extracted. The solution is then evaporated by means of a water bath, and the oily residue remaining is washed with water to remove soluble matters, then dried and weighed, and the result is the proportion of oil present in the seed.

Fig. 1.



Dr. VOHL's apparatus (Fig. 1) consists of an extractor and boiler made of glass, and connected with a condensing apparatus. The ether or other solvent is poured on the seed in the extractor, A, through which it descends to the boiler, B. The oily solution obtained is then heated, and the vap our ascends through the centre to the top of the extractor, where it is condensed by the head and cooler, and may be used over again.

The average of oil in ten samples of the following seeds was with this apparatus:—

100 Parts.	Oil.
Linseed,	27·15
Hemp,	25·87
Poppy,	49·4
Walnuts,	50·06
Almonds,	52·41
Seeds of grapes,	17·95

The part of the plant in which fats and oils are

originally produced is, according to DUMAS, the green leaves only, whence they are removed by a process of circulation, and deposited in the seeds and fruits.

In animals, fats are contained chiefly in the cellular membrane, and for the most part immediately beneath the skin; also interiorly, particularly in the omentum, and in the region of the kidneys. This substance exists in the form of globules or small drops, and swims in the animal fluid with which the cells are filled. In the species of whale, the bony cavity of the head is the depository of the secreted spermaceti; and in the case of butter, the fat is mixed in a liquid state in milk. Oils and fats, both in plants and animals, are always associated with an albuminous principle, which, from its peculiar liability to change, exercises an important influence upon the oils when kept for any length of time. The non-drying oils, on account of their containing a larger quantity of these matters, are liable to become rancid, acquire an acrid taste, nauseous odour, and redden litmus. By exhausting rancid oils with boiling water and treating them in the cold with a weak alkaline solution, they may be freed from the products of decomposition and restored to their natural state. Turned butter may thus be made equal to fresh.

PROPERTIES.—The consistence of fatty matters at ordinary temperatures is very variable—from that of extreme fluidity, as in the oil of almonds, to that of solid masses, as suet or butter. Those obtained from warm-blooded animals are usually solid at ordinary temperatures, whilst fish oils, and those procured from cold-blooded animals, remain liquid; sometimes, however, the same plant, as well as animal, yields both varieties.

Oils are neutral bodies, have a more or less viscid consistence, are almost entirely insoluble in water, but dissolve in alcohol and ether; they take fire when heated in the air, and burn with a more or less smoky flame. They are readily oxidised by any of the usual oxidising reagents.

The value of oils as combustibles is greatly affected by their degree of fluidity. This is determined by the period required for a given quantity to flow through a funnel of known dimensions. With an apparatus similar to that represented in Fig. 2, the following results have been obtained. The outlet for the oil was an aperture of 1·6 m.m. diameter.

Fig. 2.



Name of Oil.	Oil of the Seeds of	Seconds of time required to flow through a given aperture.		Fluidity Water = 100·0	
		+ 15° C.	+ 7·5° C.	+ 15°	+ 7·5°
		Seconds.	Seconds.		
Castor oil,	Ricinus communis *L.*	1800	3390	4·9	2·6
Olive oil,	Olea europæa *L.*	195	284	46·1	31·1
Gourd seed oil,	Cucurbita pepo *L.*	185	240	48·6	37·5
Hazel-nut oil,	Corylus avellana *L.*	166	218	54·2	41·2
Colza oil,	Brassica campestris oleifera *Dec.*	162	222	55·5	40·5
Rape seed oil (winter),	Brassica napus oleifera *Dec.*	159	204	56·6	44·1
Beech oil,	Fagus sylvatica *L.*	158	237	56·9	37·9
Mustard oil (from white seed),	Sinapis alba *L.*	157	216	57·3	41·7
Almond oil,	Amygdalus communis *L.*	150	209	60·0	43·0
Rape seed oil (summer),	Brassica præcox *Dec.*	148	205	60·8	43·9
Spindle-tree oil,	Evonymus europæus *L.*	143	210	62·9	42·8
Radish seed oil,	Raphanus sativus *L.*	143	197	62·9	45·6
Rape oil,	Brassica napobrassica *Mill.*	142	200	63·3	45·0
Mustard oil (from black seed),	Sinapis nigra *L.*	141	175	63·8	51·4
Poppy oil,	Papaver somniferum *L.*	123	165	73·1	54·5
Oil of deadly nightshade,	Atropa belladonna *L.*	118	157	76·2	57·3
Sunflower oil,	Helianthus annuus *L.*	114	148	78·9	60·8
Oil of Scotch fir seed,	Pinus silvestris *L.*	107	151	84·1	59·6
Cress seed oil,	Lepidium sativum *L.*	103	130	87·3	69·2
Grape seed oil,	Vitis vinifera *L.*	99	128	90·9	70·3
Plum kernel oil,	Prunus domestica *L.*	93	132	96·7	68·1
Tobacco oil,	Nicotiana tabacum *L.*	90	122	100·0	73·7
Oil of honesty,	Hesperis matronalis *L.*	89	112	101·1	80·3
Walnut, or nut oil,	Juglans regia *L.*	88	106	102·2	84·9
Linseed oil,	Linum usitatissimum	88	104	102·2	86·5
Hemp seed oil,	Cannabis sativa *L.*	87	107	103·4	84·2
Weld seed oil,	Reseda luteola *L.*	73	96	103·7	93·7

The specific gravity of oils and fats is always below that of water, and varies from 0·91 to 0·94 at 60° Fahr. (15°·5 C.). The oils, of all fluids, expand the most by heat, and, indeed, in some cases to such a degree as to render it necessary, for the purposes of commerce, to know exactly the extent of this expansion. The following table, given by SAUSSURE, shows the density of several oils at different temperatures:—

	At 53° Fahr.	At 70° Fahr.	At 122° Fahr.	At 200° Fahr.
Nut oil,	0·928	0·919	—	0·871
Almond oil,	0·920	—	—	0·863
Linseed oil,	0·939	0·930	0·921	0·881
Castor oil,	0·970	0·957	—	0·908
Olive oil,	0·919	0·911	0·893	0·862

For every degree of Celsius the volume of olive oil increases, according to Preisser, $\frac{1}{1200}$th, of rape oil $\frac{1}{1120}$th, and of train oil $\frac{1}{1000}$th, so that 100 measures of train oil at 32° Fahr. will become in summer at 68° Fahr. 102 measures.

Common hog's lard at 60° Fahr. (15·5 C.) has a specific gravity of 0·938 in its fluid state; at 122° it is 0·892; at 155° it is 0·881; and at 200°, 0·863. The specific gravity of oil increases also with its age; indeed, it may be remarked, that no accurate determination of the degree of purity of an oil can be deduced from its density, as there are frequent discrepancies in the same kind of oil, according to the locality where the plant was cultivated, and the varied modes of extracting the oil.

The annexed table, from Watt's "Dict. of Chemistry," gives the specific gravities and points of solidification of the oils in common use.

Name of Oil.	Plant.	Specific Gravity.	Solidifying Point.
DRYING OILS.			Degrees C.
Cress seed,	Lepidium sativum,	0·924	— 15
Deadly nightshade,	Atropa belladonna,	0·925	— 27·5
Gold of pleasure,	Camelina sativa,	0·93075	— 19
Gourd seed,	Cucurbita pepo,	0·9231	— 15
Grape seed,	Vitis vinifera,	0·9202	— 11
Hemp seed,	Cannabis sativa,	0·93075	— 27·5
Oil of honesty,	Hesperis matronalis,	0·9232	Below — 15
Linseed,	Linum usitatissimum,	0·93515	Below — 20
Oil of madi,	Madia sativa,	0·9286	Below — 10
Poppy,	Papaver somniferum,	0·92702	— 18
Sunflower,	Helianthus annuus,	0·92504	— 16
Scotch fir seed,	Pinus sylvestris,	0·9312	— 30
Silver fir cones,	Abies picea,	0·926	—
Spruce fir,	Abies excelsa,	0·9283	Below 15
Tobacco seed,	Nicotiana tabacum,	0·9232	— 15
Walnut,	Juglans regia,	0·92878	— 18
Weld seed,	Reseda luteola,	0·9358	Below — 15
NON-DRYING OILS.			
Almond,	Amygdalus communis,	0·91844	— 21
Beech nut,	Fagus sylvatica,	0·923	— 17·5
Seed of	Butea frondosa,	0·917	+ 10
"	Calophyllum inophyllum,	0·942	+ 5
Castor oil,	Ricinus communis,	0·9639	— 18
Cotton seed,	Gossypium barbadense,	0 9306	—
Colza,	Brassica campestris oleifera,	0 9136	— 6·25
Croton,	Croton tiglium,	0 94263	—
Cyperus grass,	Cyperus esculentus,	0·918	—
Daphne,	Daphne mezereum,	0·914	—
Earth nut,	Arachis hypogœa,	0·918	—
Ergot,	Secale cornutum,	0·922	— 37
Hazel nut,	Corylus avellana,	0·91987	— 19
Henbane,	Hyoscyamus nigra,	0·913	—
Horse chestnut,	Æsculus hippocastanum,	0·915	+ 8
Mesua seed,	Mesua ferrea,	0·954	+ 5
Black mustard,	Sinapis nigra,	0 92102	Below 0
White mustard,	Sinapis alba,	0·93383	Does not solidify
Seed of	Nigella sativa,	0·92	+ 2
Root and seed of	Pinus quadrifolia,	0·935	—
Parsley,	Petroselinum sativum,	1·078	Does not solidify at — 12
Plum kernel,	Prunus domestica,	0·9127	— 8·7
Seed of	Pongamia glabra,	0·915	+ 8
Summer rape seed,	Brassica præcox,	0·91555	—
Winter rape seed,	Brassica napus,	0 91648	Below 0
Sesamé	Sesamum orientale,	0 92415	— 5
Spindle tree,	Evonymus europæus,	0·95717	— 12
Spurge,	Euphorbium lathyris,	0·92613	— 11·25

Fats and oils may be exposed to a considerably high temperature without suffering any important change; but at a heat of between 500° and 600° Fahr. they are rapidly decomposed, and, therefore, will not admit of distillation. This property especially distinguishes the fixed from the essential or volatile oils, which can be distilled without alteration. The continued action of heat upon fat oils has a very remarkable effect. A little above 500° Fahr. they assume a darker colour, and evolve acrid and offensive vapours; and when further heated to about 600° give off carbonic acid and carburetted hydrogen gases, accompanied by a peculiarly irritating substance termed *acrolein* (C_3H_4O), various volatile organic acids, and solid and liquid hydrocarbons. The result of the action of heat, however, is not always the same, but varies with the nature of the oil. The period at which these alterations occur has been improperly called the boiling point, the phenomena of apparent ebullition arising from the escape of the gases produced by the decomposition of the oil. When introduced in small portions into red-hot vessels, or what is the same thing, when the vapour of oils is made to pass slowly through a red-hot tube, they are almost entirely converted into volatile products, consisting principally of carbonic oxide, and gaseous, liquid, and vaporous hydrocarbons. This mixture constitutes *oil gas*, which in

illuminating power is far superior to that of the best coal gas, and exceeds in this property three and a half times that of ordinary coal gas.

Excluded from air, oils may be preserved unchanged for a lengthened period; but when exposed to the air some oils, through the absorption of oxygen, become converted into a thick and viscid mass; others are changed into a transparent resinous body or varnish, especially when they are in thin strata. This reaction constitutes another well-marked distinction of the oils into the two classes, *non-drying* or *greasy* oils, and *siccative* or *drying*. The former class, though they may acquire more colour and solidity, never lose their property of communicating a greasy stain; and the latter do not solidify when mixed with nitrous acid or mercuric nitrate. Oleic acid, as obtained from drying oils by absorption of oxygen, dries to a resinous mass, like the oil from which it is derived, and appears to be a distinct substance from the oleic acid of non-drying or greasy oils. The most important drying oils are those of linseed, poppy seed, grape seed, and nuts; and all are much more susceptible of the change after having been heated with the addition of a small quantity of oxide of lead. The principal non-drying oils are those of olive, colza, sweet almonds, rape seed, and palm oil. These, when heated with plumbic oxide, turn rancid, become thick and less combustible, and acquire an offensive smell, more especially when they contain much impurity, such as albumen or mucilage.

SAUSSURE, who particularly investigated this action of air or oxygen on oils, found that recently-expressed fixed oils are scarcely affected by the oxygen of the atmosphere, but that after a variable period, sometimes of several months, but dependent upon temperature and exposure to light, they begin rapidly to absorb oxygen, and evolve hydrogen and carbonic acid gases. SAUSSURE'S experiment to prove the absorption of oxygen by oil was the following:—A layer of nut oil, one quarter of an inch thick, and 3 inches in diameter, was inclosed in oxygen gas standing over quicksilver. During eight months, from December to August, the oil absorbed only three times its bulk of gas, but in the course of ten days in the latter month it absorbed sixty additional volumes. This absorption of oxygen diminished progressively, and at the end of three months entirely ceased, and the oil had taken up 155 times its bulk of the gas. No water was generated, but twenty-two volumes of carbonic acid were disengaged, and the result was a transparent jelly, which did not produce a stain on paper.

Linseed oil, in undergoing this metamorphosis, does not evolve any gas.

Under certain circumstances the alteration by the action of oxygen becomes so energetic as to lead to a considerable elevation of temperature, and ultimate inflammation; and particularly if the surface of the oil is greatly extended, as in the case of oily wool or hemp, or greasy cloth, which, when left in a heap, has frequently taken fire spontaneously, and caused the destruction of mills, warehouses, and ships. In illustration of these occurrences, it may be proved experimentally that if paper, linen, tow, wool, cotton, or bodies of a like nature, be slightly imbued with linseed or hempseed oil, and placed in contact with sun and air, especially when in heaps or piles, they will quickly inflame.

Vegetable Non-drying Oils.—The subjoined is a list of the principal greasy oils of commerce, with the plants that yield them, their specific gravity, and the percentage amount of oil that may be extracted from some of the seeds mentioned:—

Name of Oil.	Plants.	Specific Gravity.	Yield of Oil Per Cent.
			From Olives—
Olive oil,	Olea europæa,	0·9176	30 to 36
			From Seeds—
Rape seed oil,	Brassica campestris et napus,	0·9136	30 to 36
Colza oil,	Brassica campestris oleifera,	0·9136	36 to 40
Summer rape seed oil,	Brassica præcox,	0·9390	36 to 40
Almond oil,	Amygdalus communis,	0·9180	28 to 54
Cocoa-nut oil,	Cocos nucifera,	—	—
Palm oil,	Cocus butyracea vel avoira elais,	0·9680	—
Teel oil,	Sesamum orientale,	—	40
Oil of behen or ben,	Guilandina mohringa,	—	—
Beech oil,	Fagus sylvatica,	0·9225	15 to 17
Oil of mustard	Sinapis nigra et arvensis	0·9160	15 to 38
Plum kernel oil,	Prunis domestica,	0·9127	33·3
Butter of cacao,	Theobroma cacao,	0·8920	—
Laurel oil,	Laurus nobilis,	—	—
Ground nut oil,	Arachis hypogœa,	0·9242	60
Piney tallow,	Vateria indica,	0·9260	—
Oil of radish seed,	Raphanus sativus oleifera,	0·9187	50
Cherry-stone oil,	Prunus cerastus,	0·9239	—
Apple seed oil,	Pyrus malus,	—	—
Spindle-tree oil,	Evonymus europæus,	0·9380	—
Cornel-berry-tree oil,	Cornus sanguinea,	—	—
Oil of the roots of cyper grass	Cyperus esculenta,	0·9180	—
Henbane seed oil,	Hyoscyamus niger,	0 9130	—
Horse-chestnut oil,	Æsculus hippocastanus,	0·9270	2 to 8

Characters of the Drying Oils.—The drying oils vary from those just enumerated by becoming gradually converted into solid masses by exposure to the atmosphere, and also by not being solidified by contact with nitrous acid or mercuric nitrate. Their principal use is in the preparation of varnishes and

painters' colours, and the more quickly they become hard by exposure, the more valuable are they for these purposes. Their siccative properties are much increased by heating them with various substances, (such for instance as litharge), which promote their absorption of oxygen. Oxide of manganese, oxide and sulphate of zinc, and magnesia are also used to produce a similar effect; what is technically known as *boiled* oil being linseed oil which has been thus treated. Dumas and others consider the effect to be due, in a great measure, to the presence of oleate and stearate of lead dissolved in the oil.

According to Chevreul, the common practice of heating the oil to a very high degree, and for a considerable length of time, is not essential to the production of a good drying oil; linseed oil heated to 140° Fahr., with the addition of 10 per cent. of its weight of oxide of manganese, drying very rapidly.

Liebig is of opinion that the increased rapidity with which oil thus treated becomes hard on exposure, is owing to the separation of the mucilaginous and other matters by the oxide of lead, and that the atmospheric oxygen is thus brought more closely into contact with each particle of oil. The formation of varnish is thus reduced to a simple purification of the oil, by removing all those substances which prevent the immediate contact of the oil with atmospheric oxygen.

Adopting this assumption, Liebig devised a method for removing the mucilaginous impurities by precipitation at the ordinary temperature. He recommends that the oil be agitated for some time with a mixture of water, litharge, and subacetate of lead, without the application of heat. In prosecuting his process the basic acetate of lead is first prepared as follows:—1 part of neutral acetate of lead is dissolved in 5 parts of water, and to the solution is added 1 part of finely reduced litharge. The whole is allowed to digest until the red of the litharge has been replaced by a white colour. The clear solution of basic acetate is then decanted, and mixed with an equal quantity of water, and added to 20 parts of linseed oil, which has previously been triturated with one part of finely powdered litharge. The mixture now requires to be shaken at intervals, and subsequently allowed to remain at rest for some hours, when the impurities subside with the water, and the supernatant oil is so pure that it dries into a varnish in twenty-four hours. In this case a small quantity—4 to 5 per cent.—of oxide of lead is retained in solution by the oil; but contrary to its effect after being boiled with the oil, it improves, rather than deteriorates, the varnish produced. Should it, however, in any way interfere with the uses to which the oil is to be applied, it may easily be removed by agitation with dilute sulphuric acid. The solution of acetate of lead employed in the above method of purification, and which collects below the stratum of oil, may be again used in the preparation of the sub-acetate, by the addition of litharge as before.

Enumeration of Drying Oils.—The following is a list of the principal drying oils, with their sources, specific gravity, and the percentage yield of some of the seeds:—

Name of Oil.	Plants.	Specific Gravity.	Percentage Yield.
Linseed oil,	Linum usitatissimum et perenne,	0·9347	11 to 22
Nut oil,	Corylus avellana et juglans regia,	0·9260	60
Poppy oil,	Papaver somniferum,	0·9243	56 to 63
Hempseed oil,	Cannabis sativa,	0·9276	14 to 25
Castor oil,	Ricinus communis,	0·9611	25
Grape seed oil,	Vitis vinifera,	0·9202	—
Cucumber oil,	Cucurbita pepo et melapepo,	0·9231	—
Sunflower oil,	Helianthus annuus et perennis,	0·9262	15
Tobacco seed oil,	Nicotiana tabacum et rustica,	0·9232	—
Oil of julienne,	Hesperis matronalis,	0·9281	18
Oil of camelina,	Myagrum sativa,	0·9252	28
Oil of weld seed,	Reseda luteola,	0·9358	—
Oil of cress seed,	Lepidium sativum,	0·9240	56 to 58
Oil of deadly nightshade,	Atropa belladonna,	0·950	—
Oil of cotton seed,	Gossypium barbadense,	—	—
Pinetop oil,	Pinus abies,	0·9285	—

Extraction of Oil from Seeds.—Most seeds containing oil yield it readily when they are submitted to strong pressure; to facilitate the operation they are, however, generally first bruised or crushed. Others require to be first heated, in order to coagulate the mucilaginous matters they contain; so that the oil, which is much less viscous, may be able to separate more easily. The oils from seeds which have not been previously heated are known as "virgin oils." They generally possess a more pleasant taste and smell than those which are derived from heated seeds.

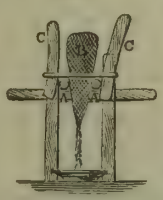
Until very recently the mode of treatment was to pound the seeds in wooden mortars with pestles shod by iron. The bruised seed was then put into woollen bags, which were wrapped in horse-hair cloth, and squeezed between upright wedges in press boxes. This process has, however, of late years been almost entirely superseded by the hydraulic oil mill and press.

Before considering the comparative advantages of the several appliances now used for expressing oil from seeds and nuts, it may be interesting to refer briefly to the methods previously adopted before the present high state of perfection in the manufacture of machinery had been arrived at. These are lucidly stated in a paper by Alexander Samuelson of Hull,* who describes historically the growth of the oil mill.

* "Proceedings of the Inst. of Mechanical Engineers," vol. iv. p. 27.

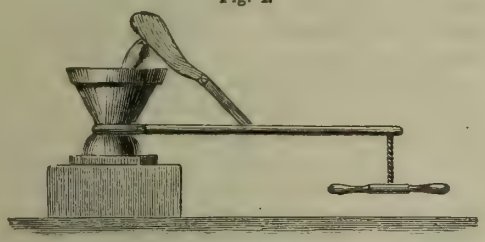
The means adopted for extracting oil in the last century originated with the natives of Ceylon, where cocoa-nuts and other seeds abound; they were of the most primitive description. The apparatus (Fig. 3) consisted of a few posts stuck into the ground, supporting two parallel horizontal bars, A A, between which was placed a bag, B, containing the seed or pulp of the cocoa-nut, from which the oil was to be expressed; levers, C C, were then brought to bear against the horizontal bars for the purpose of bringing them together, and thereby causing the required pressure upon the seed. This rude apparatus was one of the most approved oil mills of that period.

Fig. 3.



The pestle and mortar press for previously crushing the seed (Fig. 4) was also in use about the same time. The seeds were placed in the mortar, and

Fig. 4.

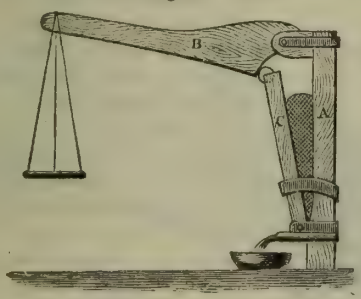


were powdered and broken up by a heavy pestle, which was carried round by the rotation of a long arm to which it was attached.

This rude mill was improved upon by HEBERT, who constructed what was considered at that time a powerful and effective machine, combining simplicity and cheapness with economy of labour.

It consisted of an upright post, A (Fig. 5), fixed firmly into the ground, the stumps of a tree being often used, upon the lower and upright ends

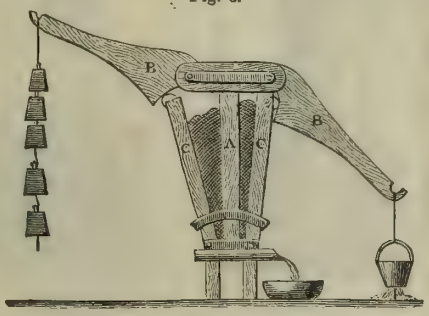
Fig. 5.



of which were projecting pieces, the upper one forming the joint of the long horizontal lever, B, and the lower one the joint of the short vertical lever, C, at the top of which was fixed a roller bearing against the under-side of the horizontal lever, B, for the purpose of diminishing the friction when pressure was exerted upon the seed. The fixed upright post, A, and the vertical lever, C, in this instance formed the compressing portion of the machine. The pressure was obtained by the weight of a man suspended from the end of the horizontal lever, B, or by loading up a scale pan fastened to the same point.

A double machine was also constructed on the same principle, and is shown in Fig. 6. The pressure was obtained either by weights or by a bucket full

Fig. 6.

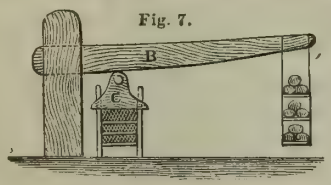


of water, which was made self-acting, in so far that as soon as the bucket touched the ground a valve was opened and the water escaped, thereby relieving the seed from any further pressure. The same letters apply as in Fig. 5.

The advantage of the double machine was that it could be made portable, so as to be moved about at pleasure, one half of the press counterbalancing the other when both sides were in action, and thus rendering it independent of the ground.

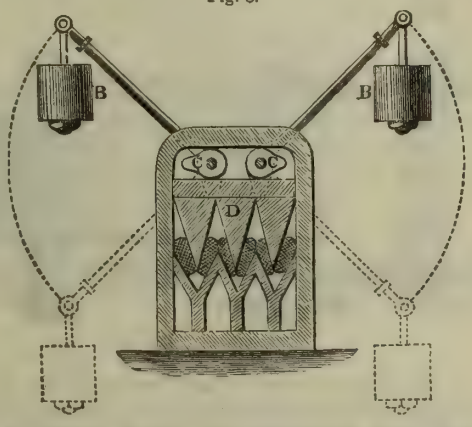
Another appliance of a similar description is shown

Fig. 7.



in Fig. 7, the only difference being that in this instance there is only one lever, B, and the seed

Fig. 8.



bags, instead of being placed vertically, were placed horizontally in a box, C, upon the loose head of

which the action of the lever was brought to bear by the same means of animate or inanimate weights.

There is also another press worthy of notice which is shown in Fig. 8, the lever and cam press. The

Fig. 9.

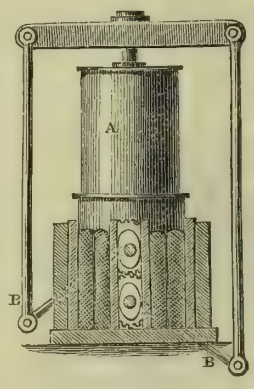
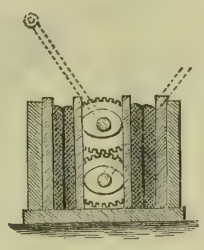
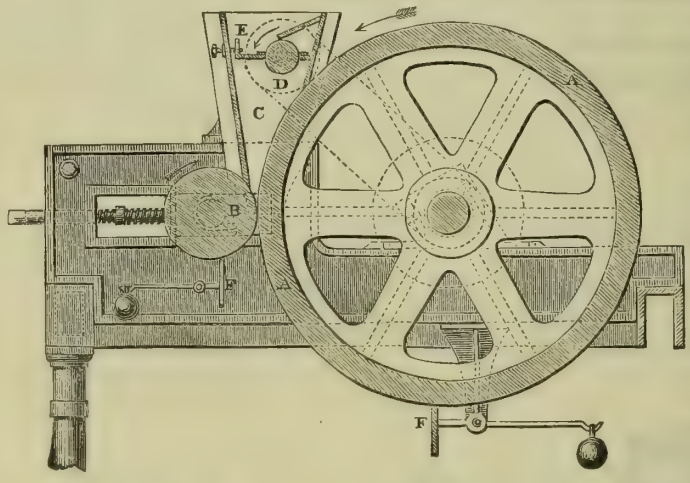


Fig. 10.



pressure is here gained by levers and weights, B B, as in most of the foregoing examples; but with this modification, that cams, C C, and wedges, D, are introduced.

Fig. 11.



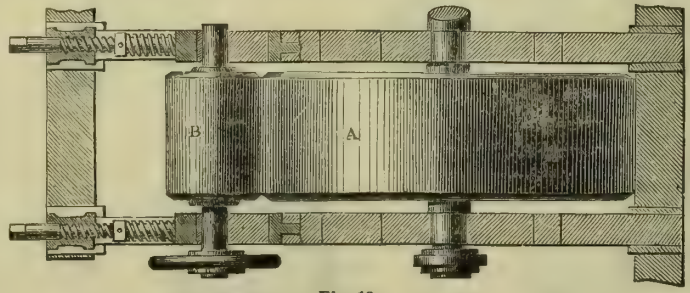


Fig. 12.

A modification of this combined lever and cam machine was invented by JOHN HALL, of Deptford (Figs. 9 and 10); in this the pressure is applied at the ends of the lever, B, by means of a piston moving in the steam cylinder, A. This apparatus is double, consisting of two pairs of boxes, the cams being placed opposite to each other, so that the operation of compressing the seed and refilling the bags may be carried on simultaneously. Fig. 10 shows the set of the cams when the pressure is at its height.

The lever presses having been briefly examined, the more approved and modern presses for extracting oil have now to be considered.

The first operation consists in passing the seed through a flat "screen" or "shaker," which is kept in a constant state of agitation.

In the second operation the seed is passed through a pair of crushing rollers, which have the effect of bruising or crushing it so as to crack the shells.

A pair of these rollers of the most approved form is shown in Figs. 11 and 12. Fig. 11 is a transverse section, and Fig 12 a plan, of the rollers.

The two rollers are of unequal diameters, the larger one, A, being 4 feet in diameter, and the smaller, B, 1 foot in diameter, the breadth of both being 16 inches, or 14½ inches on the face. The larger roller makes 56 revolutions per minute, driving the smaller one by friction. The seed is supplied through the hopper, C, by means of a small roller, D, very slightly grooved, which is made to revolve for the purpose of feeding the main rollers, being driven by a strap from the larger roller passing over a pulley outside the hopper. The amount of feed is regulated by the regulating plate and screw, E.

Underneath the rollers are scrapers, F, kept in contact with them by weights, for the purpose of scraping off any seed adhering to the surfaces after crushing.

These rollers for a long time were made of equal diameters, but it was found that they crushed the seed neither so well nor so expeditiously as they do in their present proportions. After the equal-sized rollers were found to be inefficient, the mill known as the "Ipswich" was adopted, in which the larger roller was 6 feet diameter, and the smaller 1 foot diameter; but experience proved that when any hard substance got between the rollers, the leverage over the journals was so great that it caused much wear and tear upon these points. Seed crushers have therefore adopted by degrees the medium-sized rollers, which are found exceedingly effective, and not liable to derangement.

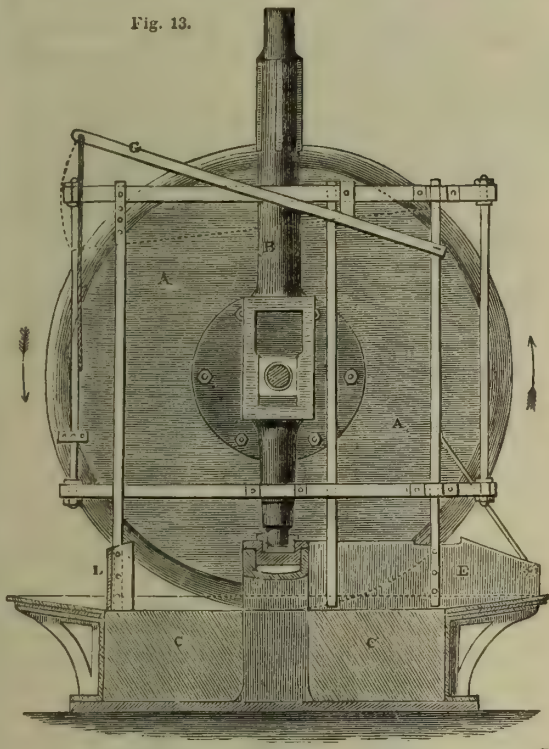
A pair of rollers such as are shown in Figs. 11 and 12 will crush upon an average about 4½ tons of seed in eleven hours, a quantity which is sufficient for two sets of hydraulic presses.

The third operation consists in grinding the seed

under a pair of edge stones, such as are depicted in Figs. 13 and 14.

Fig. 13 is a vertical section, one of the stones being removed; and Fig. 14 is a plan with one of the stones in section. The two edge stones, A A, are 7 feet 6 inches diameter and 16 inches thick, bevelled to 11½ inches broad on the face, weighing together about 7 tons. The vertical driving shaft, B, makes about 17 revolutions per minute.

Fig. 13.



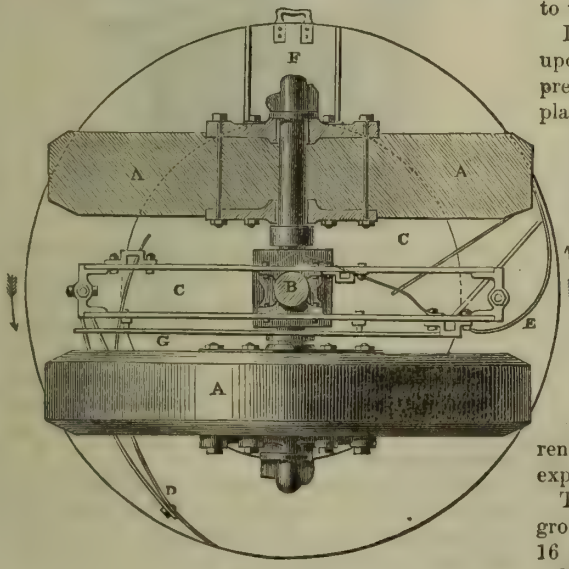
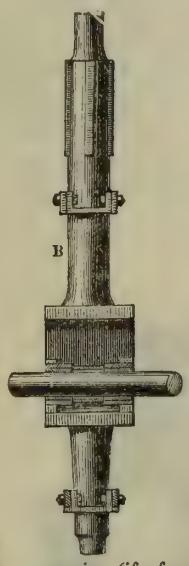


Fig. 14.

The seed is kept under the stones by means of the sweeper, D, and at the proper period is collected and swept off by a second sweeper, E, the slide or cover, F, being withdrawn for its discharge. While the grinding is being performed, the sweeper, E, is raised from the bed-plate, C, by the hand-lever, G, as shown by the dotted line. The two stones, travelling round their circular path, grind the seeds, not merely by their weight, but also by a rubbing motion or attrition; for their periphery being not conical, but cylindrical, they cannot roll on a plane surface without at every instant turning round with a certain amount of friction upon their resting points. Some manufacturers employ stones hooped with iron; but the rough granite surface is much the best. It may be dressed from time to time with hammers as it becomes irregular.

Fig. 15.



The edge stones, if of good quality and the seed not impure, require (if of granite) to be refaced about every three years, and will last from fifteen to twenty years, according to their quality.

One pair of edge stones will grind sufficient seed for two double hydraulic presses.

The process of grinding lasts for twenty-five minutes or thereabouts; the seed is then transferred to the next operation.

In some cases, and especially when operating upon old seeds, a small quantity of water is added previous to the final crushing, which, taking the place of the oil in the seed, renders the process of extraction much more easy of execution; sometimes, however, this addition would be injurious. Occasionally, also, the seeds are subjected at once to the runners, dispensing entirely with the previous crushing.

When the seed is sufficiently bruised by either or both of these operations, the pasty mass is generally heated. The object of doing so is principally to coagulate the albumen, which otherwise either retains a large quantity of oil, or itself exudes in admixture with the expressed oil. By heating the bruised seed, the oil is also rendered more limpid, and therefore more easily expressed.

The fourth operation consists in heating the ground seed in the heating kettle, shown in Figs. 16 and 17.

Fig. 16 is a vertical section of the heating kettle, and Fig. 17 a plan.

The kettle is heated by steam, and consists of two cylindrical chambers, A and B, one above the other, each of which is composed of an external casing, C, and an internal casing or inside kettle, D, with a sufficient space left between the two casings round the

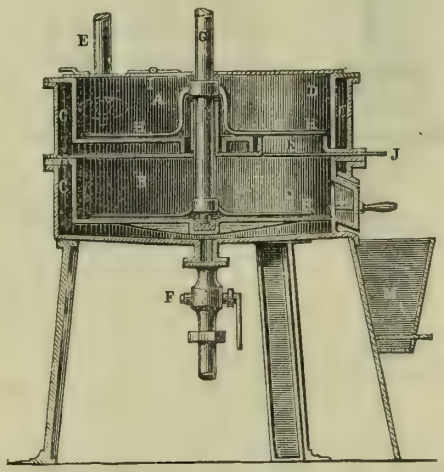
sides and at the bottom, to allow a free circulation of the steam.

The steam is admitted by the pipe, E, and the condensed water passes off at F from the bottom of the kettle.

The shaft, G, gives motion to two arms or stirrers, H H, in each chamber, revolving at the rate of 36 revolutions per minute, which keep the seed constantly agitated, so that every particle of it may come in contact with the heated sides and bottom of the kettle.

The upper chamber, A, is closed over with a sheet-iron lid, I, through which the kettle is charged.

Fig. 16.



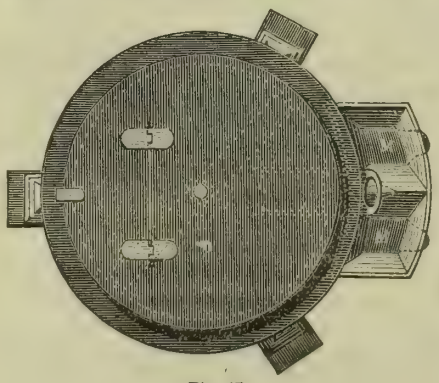


Fig. 17.

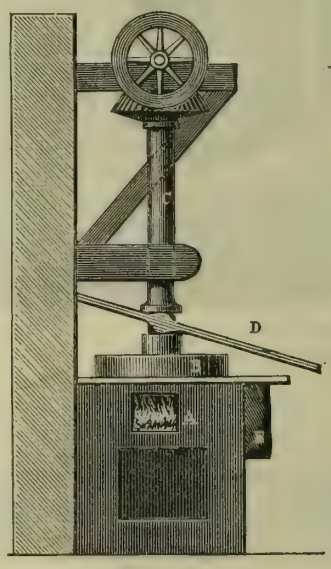
In heating the seed the upper chamber, A, is filled first, and the seed allowed to remain in it from ten to fifteen minutes; the slide, J, is then withdrawn, and the seed falls through the opening, K, into the lower chamber, B, where it remains until it is required to be taken to the press; the door, L, is then opened, and the whole of the seed is discharged from the chamber, B, by the action of the revolving stirrer, H. The seed falls through a funnel, M, under which is placed a bag of suitable dimensions to contain a sufficient quantity of seed to make a cake weighing 8 lbs. after the oil is expressed from it. Each of the chambers of the heating kettle will contain sufficient seed for charging one single press; the heating of the seed is therefore a continuous operation of first charging the upper chamber, A, and then allowing the seed to pass into the lower one, B, in which it is heated to 170° Fahr., and is then withdrawn and placed in the bags.

Another description of kettle, of a much simpler though less effective kind, is shown in Fig. 18.

In this case the seed is heated in an iron pan over an open fire, with constant agitation. A is the hot hearth, whereon the seed is placed, being confined within a loose ring, B; a spindle, C, with two arms upon it, revolves within the ring, keeping the seed stirred while it is being heated.

When the seed has become sufficiently hot, the spindle and stirrers are raised high enough above the top of the ring by the handle, D; and the ring being loose upon the hearth, the seed is drawn forward by it, and scraped into the bag, E.

Fig. 18.



By this process the seed is liable to become overheated and spoiled; and as it is exposed to the air, much heat is lost. Upon the whole, it is a costly and troublesome operation, as each ring only holds enough seed for one bag.

If fine cold-drawn oil is required, the seed-flour is subjected at once to pressure, without previously heating; but the method most commonly pursued is that given above.

The crushed cake is inclosed in a press cloth or bag previous to its introduction into the case. The bags and cloths used for this purpose are made of different materials, the object being to have them sufficiently strong to bear the force exerted; while, at the same time, they are not so thick or porous as to retain any great quantity of liquid. Woollen cloth and canvis are especially manufactured with a view to its application to this process of expression.

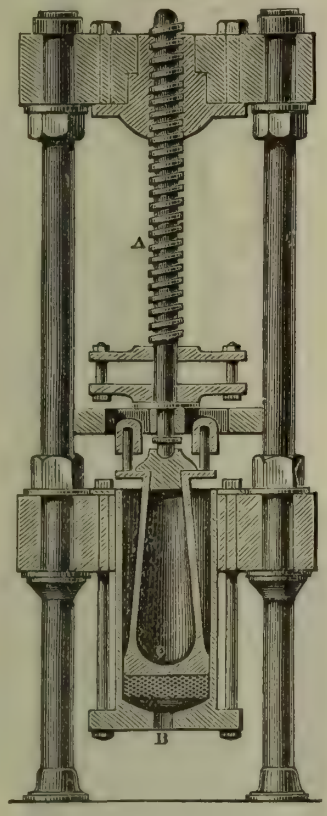
The bags, after being filled, are placed separately between what are called the "hairs," which are

bags made of horse hair, with an external covering of leather. The same description of bags and hairs are used, whether the oil be expressed by means of the stamper, screw, or hydraulic press.

Several different kinds of presses are used in the extraction of oils, as the screw press, the wedge press, and the hydraulic press.

The final operation of expressing the oil by the screw press is shown in Fig. 19, where by means of the ordinary square-threaded screw, A, the bag of seed is compressed between the bottom of the box, B, and the movable plate, C. The power is applied by means of a loose lever inserted between studs fixed in the plates, D, which are attached to the screw.

Fig. 19.



The press may be made in a vertical form, or it may be made to lie horizontally; and it may be worked either by hand or by steam or water power.

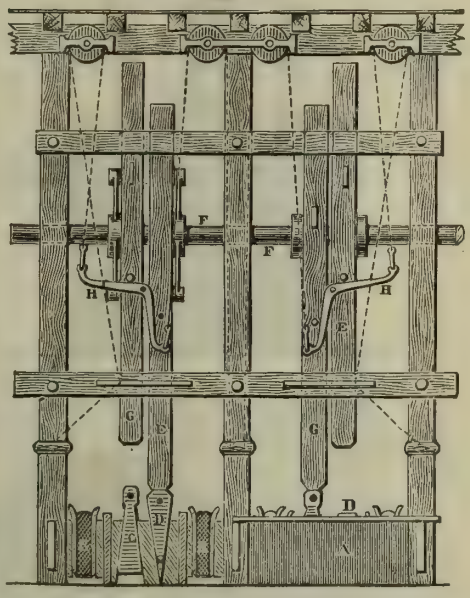
A very large amount of pressure can be obtained with one of these presses, but the wear and tear and derangement are excessive; and, besides, there are few screw presses in existence at the present day which give a correct idea of the exact proportions of oil to seed and pressure applied.

The stamper press is shown in Fig. 20. It consists of a long rectangular cast-iron box, A (shown in section in half the engraving), open at the top, at each end of which there are two plates, between which one bag of seed, B, is placed, yielding a cake weighing 9 lbs.; next to one of the inner plates is placed a filling-up piece; then an inverted wedge, C; then another filling-up piece, after which is introduced the vertical driving wedge, D; and lastly, another filling-up piece is inserted between the driving wedge and the inner plate.

As soon as the bags, B, have been placed vertically in the press-box in the usual manner, a stamper, E, made of wood, about 16 feet long and 8 inches square, with a fall of about 22 inches in the final stroke, is allowed to fall at the rate of 15 strokes per minute, for the period of about six minutes, upon the head of the driving wedge, D, which is sufficient to drive it down level with the top of the press-box, A, the stamper being worked by two cams or wypers in the revolving shaft, F.

Side by side with the stamper, E, is a second stamper, G (immediately above the inverted wedge, C), which is held suspended at a fixed point by means of the lever, H, while the first stamper, E, is

Fig. 20.



in action. But as soon as it is time to remove the bags, the stamper, E, is raised by means of the lever, H, above the point at which the cams come in contact with it; and by the same means the stamper, G, which was previously suspended, is allowed to fall upon the inverted wedge, C, driving it downwards, and thereby releasing the working wedge, D, so that the attendant workman may remove the bags and repeat the operation.

The plates are each provided with three side ribs; the immovable ones press against the sides of the case, and the movable against the intermediate wedges; and they are pierced with numerous apertures to allow the oil to percolate more easily.

A press such as that described above will not make more than about 12 cwts. of cake per day.

As the product of oil is, to a certain extent, proportional to the intensity of the pressure, it is more economical to employ that kind of apparatus which

gives the most power. The use of either vertical or horizontal hydraulic presses is, therefore, to be preferred to the form of press above described. An important improvement in this press, as used for the expression of oil, has been introduced some time, and consists in the employment of double-sided presses, and into the division between the two walls steam is introduced. The press being thus heated renders more easy the extraction of the oil.

The hydraulic press is simply Bramah's press arranged specially for the purpose of expressing oil. It has now been in use for this purpose about fifty years, although the earlier presses were very defective, as compared with those in use at the present time.

Fig. 21.

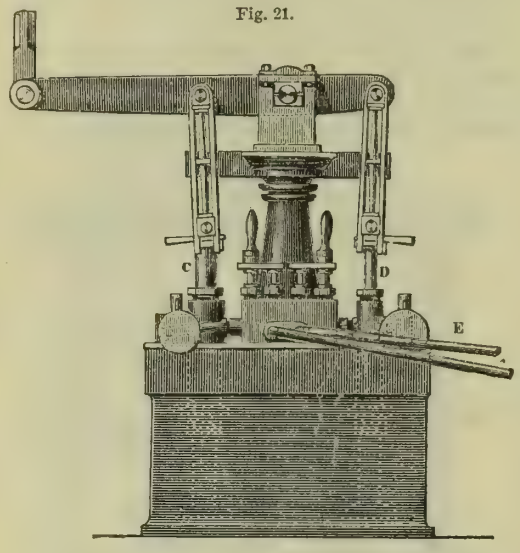


Fig. 22.

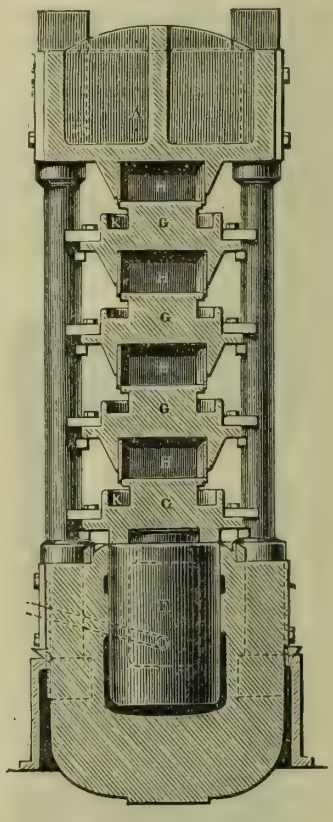
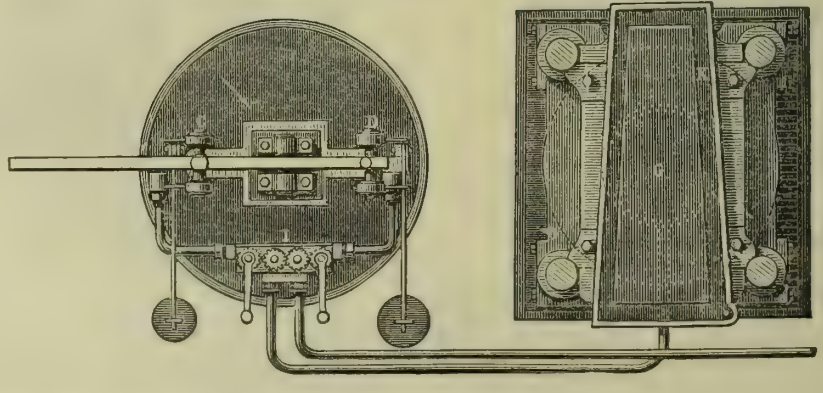


Fig. 23.



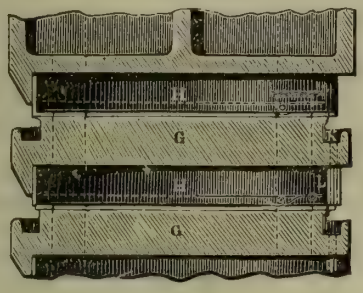
One of the first hydraulic presses that was constructed contained only one press and one set of small pumps. The box which received the seed was in one piece. It ran upon a small tramway for the purpose of withdrawing from the press to remove the cakes and replenish the bags; each time therefore that the press was put to work, the entire box had to be withdrawn, in order to empty and replenish it. It had then to be replaced upon the ram and lifted bodily upward, to bring it into contact with the press head. The constant withdrawal and lifting of this heavy box must evidently have cost much time and power.

Blundell's hydraulic press is given in Figs. 21, 22, 23, and 24.

Fig. 21 is an elevation of the pumps; Fig. 22 is a vertical section of the press; Fig. 23 is a sectional plan of the press with a plan of the pumps; and Fig. 24 is a longitudinal section through the press boxes.

The double hydraulic press consists of two distinct presses supplied by two pumps, C, D, one of which

Fig. 24.



is 2½ inches diameter and the other 1 inch diameter; both are connected to each distinct press cylinder by means of the two hydraulic tubes, E.

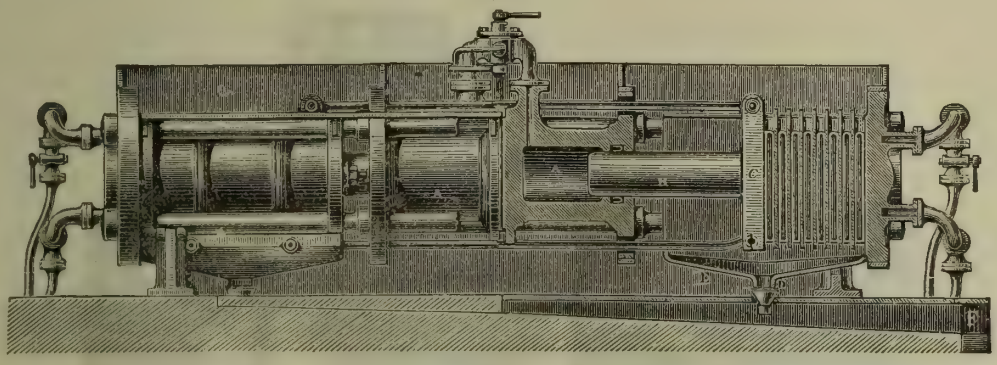
The stroke of each pump is 5 inches, and they make 36 strokes per minute; the larger pump, C, is weighted to 740 lbs. per square inch pressure, and the smaller, D, to 5540 lbs per square inch.

The diameter of the press rams, F (Fig. 22), is 12 inches, and the stroke 10 inches. Each press is fitted with four boxes, G G, and receives four bags of seed in the spaces H H, producing in all a weight of 64 lbs. of cake at each operation.

After the heated seed has been removed from the heating kettle and placed in the canvas and hair bags, which is done as speedily as possible, so that it may retain its heat, the attendant first fills one press, and opens the communication between the large pump, C, and the charged press, A, by means of the valves, I, the safety valve of the pump, C, having been replaced in its original position. The ram in the second press (not shown in the sketch) is then raised to a corresponding position with that of the first press, when the safety valve of the pump, C, rises a second time. The communication between the large pump, C, and the second press is then closed, and at the same time a communication is opened by the valves, I, between the small pump, D, and the presses; and the extreme pressure exerted by the small pump, D, amounting to about 300 tons, is allowed to remain upon the rams for about seven minutes from the time that they were first brought into action. This, together with three minutes allowed for emptying and charging the press, is the full time required for expressing the oil in a most effectual manner.

The oil in leaving the seed passes through the canvas bag, and then through the hair bag, when it finds a free exit at the edges; thence it runs into a channel or groove, K, which passes round the upper portion of each of the press boxes, G. A communication is made from one box to another by means of piping, L, so that the oil passes from the upper boxes through the lower ones, and thence into the cistern, which is called the "spell tank," being just large enough to hold the produce of one day's work.

Fig. 25.



These oil presses are not worked with water; it has been found that fluid oil works much better, and keeps both pumps and presses in a better condition.

It is scarcely possible, if the presses are properly constructed, that they should meet with any accident; this can only occur when, through carelessness, an excessive weight is placed upon the safety valve levers, or when the valves themselves are allowed to stick through want of cleanliness, from the workman not taking care to remove the oil which sometimes becomes clotted round the valves.

Each of these presses is capable of producing 36 cwts. of cake per day of eleven hours, and the yield of oil is about 14 cwts. in the same time; this, of course, depends much upon the nature of the seed.

The cake is trimmed or pared at the edges by means of a small paring knife, after which it is put into a kind of rack to cool and dry, so that it may not become mouldy when stacked.

The oil is pumped from the small tanks into larger tanks capable of holding from 25 to 100 tons, where it is allowed to remain for some time for the purpose of settling, previous to being brought into the market.

A direct-acting horizontal oil press is shown in Fig. 25.

A is the press cylinder; B, the ram; C, the press head; the expressed oil falls into the funnel, E, and runs through the opening, D, into a cistern at F.

Many advantages, however, are attached to the use of the old form of press; for it is necessary, in order to accomplish the object efficiently, that the

press should be capable of maintaining unrelaxed the degree of compression which has been produced at each successive effort, and that it should not allow the particles, by their elastic force, to regain to any extent their original condition. This quality is possessed to a greater extent by the wedge than by the hydraulic press. The former will maintain for an indefinite length of time any degree of compression which may have been applied to the substance placed in it; but not so the latter. The pressure in the hydraulic press is communicated through a liquid, and maintained by the action of valves, and it is found impossible in practice to prevent a slight leakage, which necessarily diminishes or relaxes the force of the pressure when the pump is not in action. It is necessary, therefore, more frequently to renew the force when conducting the process of expression with the hydraulic press, than is the case with the wedge press.

The arrangement of the linseed oil mill of Messrs. MARTIN, SAMUELSON, & Co., of Hull, is shown in Figs. 26 and 27.

The main shaft, A, drives the whole of the machinery. B are the rollers (the whole of the plant has already

Fig. 26.

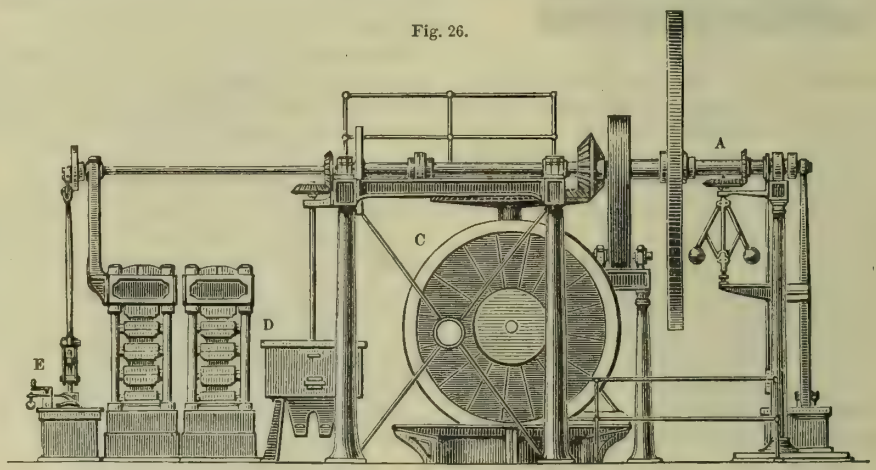
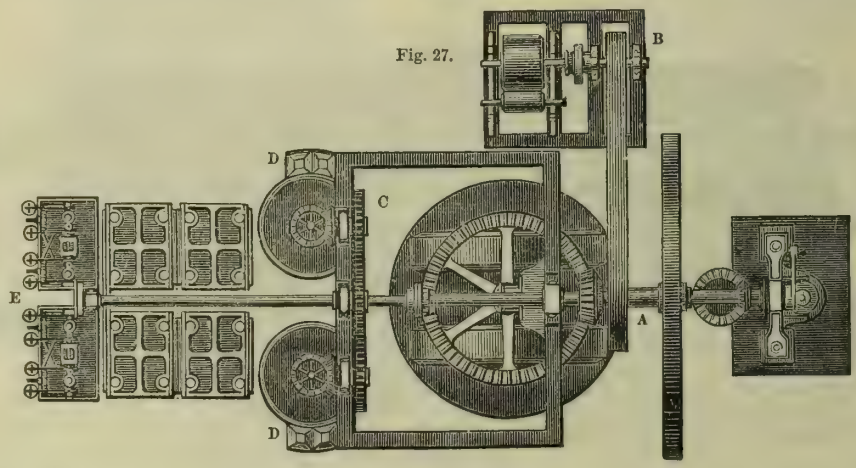


Fig. 27.



fully been described); C, the grinding edge stones; D D are the heating kettles; and E, the presses.

The oil obtained by the first expression is of the finest quality, and is kept apart from that yielded by subsequent processes. After removal of the flattened seed-cakes from the press and bags, they are returned to the millstones, and crushed and finely pulverized. The fine meal thus produced is submitted to a second compression, sometimes with the addition of a little water, and with the assistance of heat. The temperature to which it is raised is about 155°, and it is constantly agitated by a stirrer moved by machinery. The oil resulting from the compression after this process is of the second quality. In some countries, and particularly in Holland, a still further quantity of oil is extracted, otherwise the soft and fat cakes are sold as food for cattle. The last process of extraction is merely a repetition of the second, except that the pulverized cake is kept for some time at the heat of boiling water, and that a greater pressure is applied than before. The oil obtained is of the lowest quality, and the hard and dry oil-cakes cannot be applied otherwise than as manure.

E. Woolsey contributes the following valuable notes on seed crushing ("Ure's Dict." vol. iii. p. 443, 1875): "Heavy seed will yield most oil; and seed ripened under a hot sun, and when the flax is not gathered too green, is the best. The weight of linseed varies from 48 lbs. to 52 lbs. per imperial bushel; probably a very fair average is 49 lbs., or 392 lbs. per imperial quarter. I inspected one of the seed crusher's books, and the average of fifteen trials of a quarter each of the different seeds in the season averaged 14½ gallons of 7½ lbs. each. With the hydraulic press the yield is:—

Archangel seed,	15 to 16 gals.	of 7½ lbs.
Best Odessa,	18 to 19	"
Good crushing seed,	15½	"
Low seed (48 lbs. per bushel),	13½	"

Purification of Seed Oils.—Oils in their natural state are always more or less impure, and some of them so viscous as to be quite inapplicable to the lubrication of machinery, or to illuminating purposes, without previous purification. The impurities consist for the most part of albuminous, mucous, gelatinous, and colouring matters. A great part of the mucilaginous matters, and all bodies merely in a state of suspension, are deposited by repose for a sufficient length of time; but in order completely to clarify the oil, it is necessary to employ other means. The method most generally adopted is that suggested by Thénard. Sulphuric acid, for example, in the proportion of 1 or 2 per cent. of the oil, acts as a purifying agent, precipitating the mucilage and parenchymatous matters; first, by its powerful dehydrating action it removes the water by which these substances were held in solution in the oil, and afterwards chars the mucous matters themselves, thus either rendering them insoluble, or otherwise effecting their destruction. The oil itself is also to a small extent acted upon. It becomes green or dark brown, and after some time yields a deposit of the same colour, becoming itself perfectly bright and clear. Thénard's purifying process, as improved by Cogan, is conducted as follows:—The oil is heated to 212° Fahr., or thereabouts, by steam in a copper pan. In some works the steam issues through a pierced coil into the oil itself. In others a jacketed pan is used. When sufficiently hot, from 1 to 2 per cent. of sulphuric acid is gradually poured in, with constant and violent agitation. As the action of the acid depends more or less upon the amount of contact between the two liquids, as well as upon the degree of heat, it is of course desirable to employ such an apparatus as will allow the easy and rapid admixture of the oil and acid.

Cogan's improvement consists in blowing steam through the mixture. In five or ten minutes the action will be complete; and after twenty-four hours' repose the oil will be almost entirely freed from acid, and the black feculent dregs will subside, leaving the supernatant oil quite clear and greatly improved in colour. For 100 gallons about 10 lbs. of sulphuric acid are required, diluted with an equal bulk of water. At the bottom of the pan is an inverted cone, terminating in a short pipe, provided with a stop-cock inserted in its side a few inches from the bottom. After standing twelve hours, the black watery acid liquor is withdrawn by opening the stop-cock at the bottom. The clear and limpid oil is then drawn off by opening a tap in the side. What remains below this cock is turbid; and this being let out into a reservoir, is either clarified by subsidence or mixed with the next portion of raw oil. If the works are large, the oil is transferred to a cooler, so as to leave the pan free.

The quality of oils to be used for the lubrication of machinery, or for illuminating purposes, is much improved by the application of solution of tannin, by which the foreign matters are rendered more completely insoluble. In this process a strong infusion of nut-galls is mixed with the oil by agitation. After deposition, the clear oil is decanted from the precipitate, and similarly treated with a solution of acetate of lead, acetate of alumina, or sulphate of zinc, to remove any excess of tannin. During these operations the oil should be kept as near 212° Fahr. as possible. The oil is afterwards dried by agitation with freshly-calcined sulphate of lime or anhydrous carbonate of soda, which are allowed to deposit by rest. The addition of from 5 to 10 per cent. of paraffin to oils purified as above renders them much more valuable as sources of light.

A mode of treating the several varieties of rape oil has been recommended by Deutsch. His process is as follows:—The oil is placed in a copper pan or boiler, and fire-heat applied until the oil begins to be decomposed, when the heat is so regulated as to keep the oil in a uniform state of ebullition for about three or four hours. The spongy scum which separates after a time begins to subside, whilst the oil becomes clear and transparent, and of a green colour. The fire is then removed, and the oil is allowed to settle for one or two days, when the clear green oil is drawn off. If the oil has not acquired a green colour, it is an indication that the process has not been well performed, or that the oil employed was of inferior quality. The several varieties of rape oil, after this treatment, may be advantageously employed for the oiling of wool in the process of its manufacture, and they may also be employed for the lubrication of machinery. For the latter purpose, if it be desired to diminish its fluidity, a solution of caoutchouc obtained by boiling the latter in the oil may be added to the oil, which should be heated and well stirred, to effect a uniform mixture. The oil may be rendered less fluid by mixing it with tallow or other grease.

Warburton's method of effecting the purification of rape oil is by treatment with caustic alkali, in which the albuminous and other impurities are soluble, and are separated, associated with soapy matters. In a suitable vessel, containing 52 parts of caustic soda solution, of specific gravity 1·010, are to be put 100 lbs. of the refined oil; these are to be stirred with a wooden ladle till well mixed. The mixture is then allowed to stand twenty-four hours undisturbed in a cold place, after which it is then slowly warmed, and again well stirred. After

twenty-four hours' subsidence, all the oil will have separated; if such should not be entirely the case, the complete separation may be effected by the addition of a small quantity of spirit of wine. The oil drawn off from the liquor is afterwards well washed with hot water, till the pure oil is obtained without taste or colour, and, if desired, may be passed through a filter. The soap which deposits may be used as an ordinary detergent.

Non-drying Oils.—Almond Oil.—*Huile d'amandes*, French; *mandelöl*, German; *oleum amygdalæ*, Latin.—This oil is obtained by expression from the seeds of the *Amygdalus communis*, either sweet or bitter, usually from the latter, on account of their comparative cheapness, as well as of the greater value of the *marc* or pressed cake. Almonds were well known to the ancients. Hippocrates employed the expressed oil, as well as the almonds themselves, both sweet and bitter, in medicine. Dioscorides describes the method of extracting the oil.

Robiquet discovered in bitter almonds from 1 to 2·5 per cent. of a peculiar principle not contained in the sweet variety. This principle, which is termed amygdalin ($C_{20}H_{27}NO_{11}.3H_2O$), is a colourless, crystalline, nitrogenous body, with a bitter taste, and free from odour. (Bitter almond oil and hydrocyanic acid do not exist ready formed in the almond, but result from the decomposition of amygdalin under the influence of the principle emulsin).

The fixed oil of almonds is obtained by expression from either kind; and if contact of water be carefully avoided, the oil from the bitter is quite as bland as that from the sweet variety. The almonds, previously cleaned of the adherent furz and dust by being well shaken and sifted, are bruised or coarsely powdered, and pressed in hempen cloths or bags between iron plates, either cold, or, preferably, slightly and uniformly heated by hot water or steam. The yield of oil varies from 28 to 54 per cent. When recently expressed, this oil is turbid, but by rest and subsidence it becomes quite transparent. The mucilaginous matter should, however, be separated as quickly as possible, as it promotes rancidity; and the oil should be preserved in well-stopped bottles.

Almond oil is pale yellow and very fluid, inodorous when fresh, and of a faint oleaginous taste. It quickly becomes colourless by exposure to light. Its specific gravity at 15°·5 C. is about 0·918. Almond oil consists chiefly of olein, with very little solid fat; it does not solidify till it is cooled to —25° C. Cold alcohol takes up about a twenty-fourth of its weight, and boiling alcohol a sixth. It is also very soluble in ether. It very readily becomes rancid. Its principal use is in pharmacy, as an ingredient in emulsions, and occasionally in liniments, ointments, and soaps. As it contains less margarin than olive, it yields softer soap, and is better adapted to the preparation of oleic acid. The cake left after expression of the oil is sometimes ground, and is known as almond powder, and used as a detergent and for preserving the skin soft and pliable.

Bitter almonds yield, by maceration and distillation, a fragrant volatile oil, bitter almond oil, or hydride of benzoyl (C_7H_6O). This body is prepared in large quantities for use in perfumery, by simply digesting the bruised almonds in water at 30° to 40° C. for five or six hours, and then distilling the mixture. To separate the hydrocyanic acid, a dilute solution of ferrous chloride and excess of slaked lime is added to the crude oil, and the whole redistilled. The water is eliminated by shaking the essential oil with fused calcium chloride.

Commercial almond oil is frequently adulterated to a considerable extent with lard or olive oil; indeed, according to Morfit, what is sold as the genuine article is often olive oil, merely flavoured with that of almonds. According to Pereira, teel oil, or oil of *sesamum*, is occasionally substituted for almond oil, from which, however, it may be known by the deposit of margarin being formed much more readily than in oil of almonds.

Beech Oil, *Huile de faine* ($C_{15}H_{28}O_2$).—This oil is obtained from the nut of the *Fagus sylvatica*, or beech-tree. It is extracted either by cold or hot expression of the nut, previously decorticated. The percentage yield is about 16. The oil is of a clear yellow colour, is inodorous, but has a slightly acrid taste, which, however, is dissipated by keeping or by ebullition with water. Its specific gravity is 0·9225 at 15° C. At a few degrees below 0° C. it becomes solid. It combines with chlorine, forming a chlorinated oil, $C_{15}H_{26}Cl_2O_2$, and with bromine forming the compound $C_{15}H_{26}Br_2O_2$. It is not well known in this country. In some districts of France, however, it is extensively used for culinary purposes, as well as for the production of soap and as a source of light. The cake remaining after the expression of the bruised nut is useful as food for cattle.

Ben Oil, or *Oil of Behen*.—This oil is obtained by expression from the decorticated seeds of the *Mohringa nux behen*, *Guilandina moringa*, or *Moringa oleifera*, a tree resembling a willow, and indigenous to Arabia and Syria, but cultivated also in the West Indies. The oil is colourless and inodorous, and has a mild agreeable flavour. Its specific gravity is 0·912 at 15° C. By repose it separates into two portions, one thick and the other fluid at very low temperatures. The latter, as it resists the rancidifying action of the air, is highly valued for lubricating watch and clock work. The oil itself is much esteemed as an agent for the extraction of the delicate perfume of certain flowers by the process of maceration. It is also used as the base of macassar oil. Oil of ben contains a peculiar fat, named moringin, which, by saponification and decomposition of the soap, yields moringic acid. This acid is solid at 0° C. Oil of ben from *Moringa aptera* on saponification furnishes stearic acid, margaric acid, benic acid, and moringic acid.

Cacao Oil, or *Butter of Cacao*.—This substance is the fatty matter of the chocolate nut. The *Theobroma cacao* is the tree producing this nut, and is grown extensively in Demerara, Berbice, the West Indies, and South America. There are numerous species of this tree, bearing different

kinds of fruit, which differ both as to form, size, and the number of seeds which they contain. The average size of the good nuts is that of the sweet almond, but rather more thick. Those from Caracas or New Granada are especially remarkable for the large proportion of fatty matter they contain. Cocoa and chocolate are preparations of the nut of this tree, produced by roasting and grinding, and sometimes with the addition of various other ingredients, as sugar, starch, gum, treacle, arrowroot. Cacao beans contain:—

	Guayaquil.	Trinidad.
Theobromine,..	0·63	0·48
Cacao red,..	4·56	6·22
Cacao butter,..	36·38	36·42
Gluten,..	2·96	3·15
Starch,..	0·53	0·51
Gum,...	1·58	0·61
Extractive matter,..	3·44	5·48
Humic acid,..	8·57	9·25
Cellulose,..	30·50	29·86
Ash,..	3·03	2·98
Water,..	6·20	4·88
	98·38	99·84

Butter of cacao is obtained from the powdered kernels after being mixed with 10 times their weight of boiling water, by expression in canvas bags, between heated iron plates. One pound of cacao yields from 5 to 6 ozs. of oil. It is purified by long boiling with water, or on the small scale by boiling alcohol. The crude oil is yellowish and has the smell and taste of the nut. In the pure state it is colourless, inodorous, and tasteless. It is not liable to become rancid, and hence the great value of the nut as an article of diet. Its consistence is about that of tallow, and its flavour rather agreeable. Its specific gravity is 0·91; its melting point about 30° C., but does not become solid till cooled to 23° C. It is for the most part a crystalline combination of olein and stearin. Cacao butter is readily soluble in hot alcohol, but is deposited on cooling. Ether also dissolves it. It is used in France in the manufacture of soap and candles.

Cocoa-nut Oil is extracted from the kernels of the cocoa-palm—*Cocos nucifera et butyracea*—either by expression or by ebullition with water. It is of a whitish-yellow colour, and dissolves readily in oils, alcohol and ether, benzene, &c. It becomes rancid very quickly, from the large amount of mucilage it contains. The cocoa-palm is a native of tropical countries, but does not thrive except near the coast. Five varieties are indigenous to Ceylon. The bark yields a peculiar oil, used by the Cingalese in the form of ointment in cutaneous diseases.

In Malabar and Ceylon two methods of extracting the oil or cocoa *butter* are practised: the one is by pressure, the other by boiling the bruised nut, and skimming off the oil as it rises to the surface. The kernels of this palm are also brought to Europe, and the oil is extracted by the aid of heat, the fruit having been previously ground or cut into small pieces. The oil consists of a fluid and a solid fat, which are most probably distinct and separate in the seeds, but become mixed under the press, and so much the more the higher the temperature is raised; so that fluid or solid fat, or such as is of medium consistence, may be obtained as desired, according to the amount of pressure applied and the temperature at which the operation is conducted. Commercial cocoa-nut oil is concrete at temperatures below 18° C., and at about 20° C. is fluid. The solid constituent of this oil varies from that of other oils, and is named cocostearin or cocosin. The principal use of cocoa-nut oil is in the manufacture of soap and candles. As a material for the production of soap it is in many respects valuable, the soap being brilliant white, very hard and light, and to a larger extent soluble in saline and alkaline waters than most other soaps, and consequently useful for washing in salt water. Cocoa-nut oil has also been used as a therapeutic agent, and by some is considered little inferior to olive oil. On the continent of India, as well as in Ceylon, it is used as a pomatum for promoting the growth of and preserving and softening the hair. Its odour, and the rapidity with which it becomes rancid, are, however, great objections to its employment, either in medicine or as a pomatum. The olein of cocoa-nut oil, which remains liquid at ordinary temperatures, cannot be burned in an argand lamp of ordinary construction, in consequence of its charring the wick. With a view to cheapness, and to combustion in what is known as the solar lamps, it may be employed in admixture with spermaceti oil, but the latter is deteriorated in proportion to such addition. Cocoa-nut oil is a very complex fat, containing free acids, yielding many fatty acids on saponification. Some of these are:—Lauric acid, $C_{12}H_{24}O_2$; myristic acid, $C_{14}H_{28}O_2$; acids having the composition, $C_{11}H_{22}O_2$, and $C_{12}H_{26}O$; also palmitic acid and stearic acid.

Cocosin or cocostearin is separated from the liquid portion of cocoa-nut oil by pressure, by ether, or by solution in boiling alcohol, from which the stearin crystallizes on cooling, exactly as in the case of ordinary stearin (see Candle).

Laurel Oil.—This oil, termed also *oil of bays*, is imported from Trieste. It is procured from either the fresh or dried berries of the sweet bay—*Laurus nobilis*.

Laurel oil is obtained from the berries by boiling and by expression. The berries are bruised in a mortar, boiled for three hours in water, and then pressed in a canvas bag. The oil exudes with the decoction, and when cold, floats on the surface. The dried berries are steamed until thoroughly soaked, and then quickly pressed between heated iron plates. By the latter process they yield one-fifth of their weight of oil.

Laurel oil is of a greenish colour, of the consistency of butter, and of a peculiar and characteristic smell. It is partially soluble in alcohol, and completely so in ether. It consists for the most part of a peculiar variety of stearin, named *laurostearin*, or laurate of glyceryl ($C_{27}H_{50}O_4$); the residue is a green liquid fat, probably olein. Laurel oil is

saponifiable. It is occasionally employed in medicine as a stimulating liniment in sprains and bruises, and in paralysis. Its principal use, however, is in veterinary medicine.

MUSTARD OIL.—This oil is procured by expression of the bruised seeds of the black or white mustard. The mustard plant—*Sinapis*—of which there are several species, appears to be indigenous to this country. It was formerly cultivated in Durham, but is now grown principally in the neighbourhood of York. In India and the East, mustard is cultivated solely for the sake of the fixed oil it contains. The proportion of oil is about 36 per cent. of the seeds. According to the analysis of JOHN, white mustard seeds consist of an acrid volatile oil, yellow fat oil, brown resin, gum, extractive ligneous fibre, albumen, free phosphoric acid, and salts. ROBIQUET and BOUTRON, however, have proved that white mustard does not contain volatile oil, nor any substance capable of producing it. The yield of oil from white mustard seed is about 36 per cent. Oil of mustard is of a reddish or brownish yellow colour, and is nearly inodorous. It has a thick oily consistence, and may be preserved for a lengthened period without becoming rancid. Its specific gravity is about 0·916. It requires 1000 parts of alcohol at 0·90 for solution, but dissolves in 4 parts of ether. It does not congeal at low temperatures. By saponification glycerin is eliminated, and by decomposition of the soap produced, stearic acid, *erucic acid*, and an oily acid, are liberated. Erucic acid forms acicular crystals which fuse at 34° C. Its formula is $C_{22}H_{42}O_2$. Oil of mustard may be applied to the same purposes as rape oil; it has been used in the manufacture of soap, and also medicinally as a purgative and anthelmintic. The expressed mustard cake, owing to its acridity, is unfit for food for cattle, and is only useful as a manure. Black mustard seed yields 18 per cent. of a similar oil, which, however, solidifies at 0° C.

NUTMEG OIL.—The fruit of the *Myristica moschata* by expression yields this oil—known also as oil of mace. The nutmeg-tree grows to a height of 20 to 25 feet, and in appearance resembles a pear-tree. It is cultivated in the Moluccas, and in the East and West Indies. Several varieties of nutmegs are met with in commerce. Their principal consumption is for dietetical purposes.

The process employed in the extraction of the fixed oil is bruising the nut to a paste, inclosing the mass in a bag, and submitting it for some time to the action of steam. The whole is then placed between heated metal plates, and subjected to long-continued expression. The yield of nutmeg oil is about 12 per cent. of the weight of the nuts employed. It is imported in oblong cakes, covered with leaves, and weighing about 12 ozs. It is of a reddish-yellow colour, firm consistence, and possesses the agreeable smell and taste of the nutmeg. According to SCHRADER, this oil consists of 52 per cent. of a liquid, and 44 per cent. of a solid fat (myristicin, $C_{10}H_{20}O_3$), with 4 of volatile oil.

OLIVE OIL.—*Huile d'olives*, French; *olivenöl*, *baumöl*, German; *oleum olivæ*, Latin.—Olive oil appears to have been known from the remotest antiquity. The olive tree—*Olea europæa*—is one of the prettiest in nature.

Olive oil appears to have been known from the earliest times, since the method of producing it is mentioned by MOSES, and is, with slight variation, the process employed at the present day. It is obtained from the bluish or brownish-green integument, or sarcocarp, of the fruit or olives. Several varieties of olives are met with in commerce, but the most common is the small French *Olea europæa longifolia*, and the large Spanish *Olea europæa latifolia*. The ingathering is performed in different ways, according to the kind of oil to be extracted. If the olives are gathered some time before they are ripe, they yield an oil with an acrid and bitter taste. When more ripe, but still before they arrive at maturity, the oil possesses the peculiar taste of the fruit, and may be preserved for a lengthened period without becoming rancid. When fully ripened, so as to drop from the trees, they yield a fine oil, but more fatty, and also more susceptible of change by exposure. November and December are the principal harvest months, and if allowed to remain longer on the trees the olive gradually deteriorates, and yields an oil of very inferior quality. To obtain the finest oil the olives should be gathered by hand, for if bruised, as in the usual method of beating the fruit from the trees with poles, unless used directly, they ferment, and the oil acquires a highly disagreeable odour and taste.

The process for procuring olive oil is somewhat modified in different countries, though the principle is the same in all, namely, for the purest:—gentle pressure of the freshly gathered fruit in the cold; for common or second oil—stronger pressure, aided by partial fermentation of the olives and the heat of boiling water; and for another still inferior kind,—boiling the husk or *marc*, after the preceding treatment, with water, when a mucilaginous oil rises and floats on the surface. All the varieties are left to repose for a month after being extracted, in order that the impurities may subside.

The following is the method pursued in the south of France:—The ripe olives are crushed in a mill of rude construction, comprising usually a single millstone turning in a circular bed; but sometimes two millstones, placed wide enough apart not to crush the seeds, are used. The workmen remove all the pulp when sufficiently crushed, and place it in rush sacks, which are heaped up, to the number of eighteen or twenty, on the platform of a press. This is also of a very rude description, and is only capable of a very slow and feeble pressure. The oil which first exudes from the bags, when the olives are of good quality and the pressure is nicely regulated, is the variety known as salad oil, and is much in request for the supply of the table. After the first pressure the pulp still contains a considerable quantity of oil, so mixed with albuminous matters that it cannot flow out. To extract a portion of this oil the press is taken apart, the cakes are broken up in the bags,

and the nearly dry residue is digested with boiling water, and again pressed as before. The boiling water being absorbed causes the pulp to swell; the albumen coagulates, and the more fluid oil runs out freely. This operation is repeated two or three times. For the reception of the water containing the oil two tanks are used, so arranged that in one the liquids separate into two layers, whilst the other is filling. The upper layer, consisting of oil, is ladled off, and the water below, which still contains oil in suspension with mucus, is collected for further separation into a narrow and deep cistern, from which the water can be removed by a long siphon. After deposition of a portion of water it is drawn from underneath, the cistern is again filled with a further quantity of the mixture, and when a sufficient quantity of oil swims on the surface it is skimmed off, as oil of inferior quality. Owing to the imperfections of these processes a quantity of oil still remains in the refuse in the bags, and the producers of oil find it worth while to submit it to a third operation. It is evident that the use of mills of similar construction to those used for the extraction of oil from seeds, and the employment of hydraulic presses, would much increase the yield of oil and shorten the work.

The last operation, in the method usually employed, is as follows:—The cake or *marc*, after the second pressure, is immediately moistened with water as a preventive of fermentation, which otherwise quickly ensues, and effects the destruction of the last traces of oil. The absorption of water is accelerated by heaping the moistened cake in layers in vats. The next step is the separation of the stones: this is effected by means of two machines adjoining each other, and worked by the same motive power. The first consists of a vertical millstone turning in a pit of masonry or woodwork, through which flows a current of cold water. The cake passed through this is conveyed through a trap-door into the other machine of similar construction to the first, except that the crusher is heavier; and there is attached to the axle an arm, which serves to agitate the paste with the water. In this process the broken stones fall to the bottom, whilst the lighter parts, with the kernels of the seeds, rise to the surface, and are removed by means of hair sieves. These unctuous matters are dried over a fire until they form a stiff paste, which is then submitted to pressure as before. The oil thus obtained is applied to lighting purposes, and in the manufacture of soap. At the mills the fruit is often allowed to remain in heaps for some days, or until the mill is at liberty, from which cause the oil is of far inferior quality than would otherwise be obtained.

The black press water from the olive oil manufacture contains much organic matter, sometimes as much as 85 grams. per litre; and when the free acids have been neutralized with lime this residue is used as a manure.

From the residue, after extracting the oil from the pulp of the olive, which was formerly used as fuel, more oil is now extracted by carbon disulphide. The mixture is distilled, and yields olive oil and carbon disulphide for a fresh operation: 25 per cent. of oil is said to be recovered.

The olive oil thus recovered is used in the manufacture of soaps, and nearly all of it is transferred to Marseilles.

In Naples the olives when ripe drop from the trees, and are collected and conveyed to the mill. The oil when expressed is inclosed in sheep or goat skins, and carried on mules to Gallipoli, where it is allowed to clarify in reservoirs cut in the rock on which the town is built, and its ultimate value depends in a great measure on the nature of this cistern. In point of fact Gallipoli owes its celebrity to the facility of the formation of these cisterns, as in them the oil soon clarifies, and may be preserved for a lengthened period without becoming rancid.

The finest olive oil is of a pale yellow colour, sometimes inclined to green. It has scarcely any smell, but a bland, mild, and agreeable taste; occasionally it has a nutty flavour, and when swallowed leaves a slight sense of acrimony in the throat. It is insoluble in water, slightly soluble in alcohol, and in $1\frac{1}{2}$ times its weight of ether. Its specific gravity is, according to SAUSSURE, at 12° C., 0·9192; 25° C., 0·9109; 50° C., 0·8399; 94° C., 0·8624. Olive oil boils at 315° C.; at about 10° C. olive oil deposits white granules; at 0° C. it solidifies, but can by pressure be separated into a solid tallow-like substance, *oleo-margarin*, and a fluid oil, *triolein*. By saponification it is resolved into glycerin, and oleic, palmitic, and stearic acids, &c.

Of the different kinds of olive oil met with in commerce, the produce of Aix, known as Provence oil, is the most esteemed. Florence oil, imported from Leghorn in flasks, packed in chests containing thirty of these, is a very fine kind used for culinary purposes. Lucca oil is imported in jars holding 19 gallons each. Gallipoli forms the largest proportion of that brought into this country, and is imported in casks. Puglia and Calabria are the provinces of Naples most celebrated for its production. Sicily oil is principally produced at Milazzo, and is of inferior quality. In some countries, and especially on the continent of Europe, olive oil constitutes an important article of diet. It is extensively used in England in the manufactures, and especially in the treatment of woollen cloths. The inferior kinds are much used in the production of soaps, particularly of the varieties known as Marseilles and Castile soaps. Being less liable to become thick and viscid by exposure to air, it is often used for oiling delicate machinery. For application to watch and clock work, the oil is refined by cooling, separating the fluid portion, immersing in it a slip of sheet lead or some shot, and exposing it to direct sunlight in a corked phial, when a whitish matter gradually subsides, and the oil is rendered clear and colourless. This when decanted is fit for use.

A better process for purifying olive oil consists in treating the oil, heated to about 90° Fahr., with a strong solution of potash or soda. The specific gravity

of the solution may be 1·2, or even stronger. The oil is kept constantly agitated during the addition of the alkali, and the operation is at an end when a small portion of the oil placed in a glass bottle, and shaken with a further addition of solution of alkali, deposits only a clear liquid free from soapy matters. The quantity of solution of alkali required varies from 3½ to 8 per cent. The oil is decanted after deposition of the soapy matters, and passed through a filter.

Adulterations.—The superiority of olive over other kinds of oil, and its higher price, render it liable to adulteration with rape and poppy oils, and especially with lard oil—what is called *superfine* Lucca oil often containing as much as 60 or 70 per cent. of the latter. Several methods have been proposed to detect these sophistications. Poppy oil may be discovered by the phenomena of *beading*, or the appearance of a number of air bubbles on the surface after violent agitation of the oil, which are not produced with pure oil. The most reliable test is that suggested by Poutet, which depends upon the peculiar action of nitrous acid upon olive oil. He dissolves 6 parts of quicksilver in 7½ parts of nitric acid, of specific gravity 1·36, without applying heat. When 1 part of this freshly prepared solution is added to 10 parts of pure olive oil, the mixture becomes concrete in the course of a few hours. The nitrous acid or nitric peroxide converts the liquid olein into solid elaidin. The admixture of foreign oils prevents this congelation, so that the resulting mixture is more or less liquid in proportion to the quantity of the adulterant present. The 20th part of poppy oil is easily detected by this method, but in order to arrive at satisfactory results, a comparative experiment should be made with a mixture of oils of known composition.

Palm Oil.—This very important fatty oil is procured from the fruit of a species of palm—*Acoira elais* or *Elais guineensis*—cultivated on the west coast of Africa and in tropical America. It is composed of tri-palmitin, $C_{51}H_{98}O_6 = \left.\begin{matrix} C_3H_5 \\ (C_{16}H_{31}O)_3 \end{matrix}\right\} O_3$, with a very small quantity of olein. The fruit of the palm is about the size of a pigeon's egg, and of a deep orange-yellow colour. It consists of a hard stone, within which is the seed, and surrounding the nut is a fibrous, oily, yellow sarcocarp, or fleshy integument, from which, by boiling in water, the oil is separated, rises to the surface, and may easily be collected. Fresh palm oil has an orange-yellow tint, a sweetish taste, and possesses an odour somewhat resembling that of violets or orris root. It has the consistency of butter or lard, is lighter than water, and by exposure to the air quickly becomes rancid, and of a paler hue. Its melting point is variable, ranging from 27° to 36° C., and is still further heightened by age. It is slightly soluble in cold, more readily in boiling alcohol, but is deposited from the latter on cooling. In ether, it dissolves in all proportions. Palm oil was once considered of no importance in the arts and manufactures. At the present time it is exported from one port on the African coast to the amount of upwards of 20,000 tons annually, in exchange for foreign produce; and the annual consumption of palm oil in this country is upwards of 25,000 tons, which are imported in exchange for goods of British manufacture. As it occurs in commerce, palm oil is in a state of rancidity, containing free fatty acids. The characteristic orange colour of this oil is to be attributed to the spontaneous decomposition of a peculiar principle of the palm, always associated with the oil. The principal use of palm oil is, after admixture with other oils, in the production of soap and candles. In soap-making, the oil is used both bleached and as imported, according to the kind of soap required; in the candle manufacture, the solid constituent only is used, and is hardened by the addition of wax. In Africa palm oil is employed by the natives as a kind of butter. The colour of palm oil is destroyed by passing air and steam into it. The action of light was formerly thought to be necessary. The fat is turned into a huge lead-lined cistern, and air blown into it at the same time that high-pressure steam, issuing from a coil pierced with a number of holes, heats it and keeps it in constant motion. (See Soap.)

Palmitin, or tri-Palmitate of Glyceryl.—This solid fat constitutes about two-thirds of the weight of palm oil. It may be obtained tolerably pure and in large quantities by pressing palm oil. It appears as a wax-like mass, and is used in the manufacture of a variety of stearin candles, whilst the yellow fluid oil is saponified. It is obtained pure by washing the residue of the second pressure with hot alcohol, dissolving it in hot ether, and crystallizing repeatedly till the melting point becomes constant. Palmitin is insoluble in water, and only very sparingly soluble in boiling absolute alcohol, but very readily dissolves in ether. It fuses at different temperatures, according to its physical structure—viz., 46°, 61°, and 62°. It solidifies at 45°·5 C. to a friable mass similar to wax.

Rape Oil, *Huile de Navette.*—This oil is prepared from the seeds of several species of the genus *Brassica*, belonging to the family of *Cruciferæ*, as the *Brassica napus*, or winter rape, and the summer rape, or *Brassica præcox*. Besides oil and woody fibre, these seeds contain a considerable quantity of mucus, albumen, and other allied substances. Only the driest possible seeds, such as have been stored for several months, and protected from moisture, are expressed. It is usual also to submit the seed to steam heat previous to pressure, as, if the albumen present is not completely coagulated, the oil obtained is much less in quantity, and far inferior in quality, to that otherwise extracted. The very large proportion of fluid contents, other than oil, contained in fresh seed, constitutes the great difficulty in obtaining an average oil both as to quantity and quality; but by the above method of treatment this obstacle is overcome, and the oil expressed, containing only a trace of albumen, and a greatly-reduced proportion of mucus, becomes comparatively easy of purification. As newly expressed, even with every precaution, it is viscid, owing to the mucus and other foreign

matters unavoidably present. These, and the colouring matter also retained by the oil, lessen its combustibility, and occasion much smoke during its burning.

The *Brassica napus* yields about 33 per cent. of oil.

3½ lbs. of best rape seed yield 1 lb. of oil.
3¾ lbs. of common rape seed yield 1 lb. of oil.

The imperial bushel of rape seed contains 52 to 56 lbs., according to quality. Rape oil from *Brassica napus* is of a bright yellow colour; at 15° C. its density is 0·9128; it solidifies below 0° C. The oil from *Brassica præcox*, or summer rape, is more viscid; its specific gravity at 15° C. is 0·9139; it deposits a fat at —8° C, and solidifies at —10° C. (Schubler).

Purification.—Rape oil is most conveniently purified by Thénard's process, as modified by Cogan, which has been already described. See Purification of Oils.

Rape oil is employed in the manufacture of woollen goods, in the preparation of some kinds of leather, for oiling machinery, in the production of soap, and also for burning. According to Brotherton, a manufacturer of oils, good English-grown rape seed yields oil of superior quality to any foreign seed ever brought to his notice, and he consequently recommends its cultivation to agriculturists. The inferiority of the oil obtained from Indian or colonial seed probably depends, in a great measure, on the want of sufficient care being paid to the purity and cleanness of the seed itself, and not to any real deficiency in the oil.

Colza oil is extracted in the same manner as the preceding from another variety of seed of the same genus of plants—the colza, or wild navew, *Brassica campestris oleifera*. It is produced in France in large quantity, and is used for the same purpose as rape oil. It is of a yellow colour, and nearly free from odour. Its specific gravity is 0·9136 at 15° C. It congeals at about —6° C. It is sparingly soluble in cold alcohol, but readily soluble in this fluid when assisted by heat. It is chiefly a mixture of two glycerides, which on saponification yields brassic acid, and an acid resembling oleic acid. Brassic acid melts at 33° C., and crystallizes from alcohol in long needles. Colza oil is largely used for illuminating purposes, and may be burned without previous purification.

A Parisian named Nuerberger, in 1856, obtained a patent for the extraction of oil from the seeds of other genera of the order *Crucifera*. This oil forms a substitute for colza oil, and may be used for lighting and other purposes. The three genera from which the oil may be procured are the genus *Thlaspi*, or shepherd's-purse; the genus *Capsella*, or common shepherd's-purse; and the genus *Iberis*, or candy-tuft. The species *Capsella bursa pastoris* yields the largest proportion of oil. The latter is obtained precisely as colza oil, and is also purified in the same manner.

Teel Oil, or *Oil of Sesame*, $C_{10}H_{18}O_2$ (Lefort).—The plant yielding this oil, the *Sesamum orientale*, is extensively cultivated throughout India for the sake of the fine oil expressed from its seeds, which is used for food, for soap-making, and for burning in lamps. The latter are imported from Calcutta under the name of teel seeds. They are about the size of white mustard seeds. Three varieties are known—namely, the white, the parti-coloured, and the black. It is principally from the latter that the sesamum oil of commerce is obtained. The seed contains about 45 per cent. of oil. Oil of sesame does not become solid by exposure to air: its colour is pale yellow. Specific gravity 0·9230 at 15° C.; at —5° C. it becomes a fat.

Drying Oils.—The drying oils differ from those above described, by their peculiar behaviour on exposure to the air, and also, as previously noticed, by the difference in their behaviour under the influence of nitrous acid. The cause of the singular property of drying in contact with atmospheric air is not distinctly understood, but is usually attributed to some peculiarity in their olein.

Castor Oil.—*Huile de ricin*, French; *ricinusöl*, German; *oleum ricini*, Latin. This oil is extracted from the seeds of the *Palma christi*, or common ricinus, which is cultivated in the East and West Indies, and in the United States of America.

The plant yielding this oil was known in the most ancient times. The Egyptians were certainly acquainted with it, as Caillaud discovered its seeds in some Egyptian sarcophagi conjectured to have been upwards of 4000 years old. It was known to the ancient Greeks, and is alluded to by Herodotus and by Hippocrates, the latter of whom employed its root in medicine. The Latins gave it the name of *ricinus*, whence its botanical appellation. In this country the *Ricinus communis* is an annual, and seldom exceeds 4 feet in height. In other countries it is perennial, arborescent, growing to the height of 15 or 20 feet. It has large vine-shaped leaves, green spikes of flowers, and rough capsules containing ovate shining black seeds, spotted with grey.

Extraction of the Oil.—Various methods have been adopted for the preparation of castor oil. The expression of the seeds in the cold, though a more tedious process, yields a much superior oil to that obtained when the pressure is assisted by heat. Previous to expression the seeds should be deprived of the outer coating or shell, when they yield an oil nearly colourless, or with a slight yellow tint.

According to Soubeiran, Bussy, and Lecanu, all processes in which heat is employed are objectionable, as the oil is rendered acrid from the liberation of fatty acids. In the American Pharmacopœia, on the contrary, the application of heat is stated to improve the oil by volatilizing a disagreeable acrid principle; and hence the almost universal practice in America is first to submit the seeds to gentle desiccation, the heat being kept too low to scorch or decompose them. They are then introduced into a powerful screw press, and submitted to pressure. A whitish oily liquid exudes, which is boiled with a considerable quantity of water in iron boilers, and the impurities skimmed off as they rise to the surface. The coagulated albumen forms a layer between

the oil and the water, and the starch and gum are retained in solution in the water. The clear oil is next drawn off and boiled with a small quantity of water until steam ceases to rise, and till a small portion of the liquid taken out in a phial preserves a perfect transparency on cooling. The effect of the latter operation is to clarify the oil, and render it less irritating, by driving off volatile acrid matter, the quantity of which is doubtless much increased by the process of torrefaction to which the seeds are subjected. The process of cold expression, purification by subsidence and decantation, is also employed in America, though on a much less extensive scale.

In England castor oil is expressed by Bramah's hydraulic press, or by the common screw press, in a room artificially heated. It is purified by rest, decantation, and filtration, and bleached by exposure to light on the tops of warehouses.

In Calcutta the process is as follows:—The fruit is shelled by women; the seeds are bruised between rollers, then placed in hempen cloths, and pressed in the ordinary screw or hydraulic press. The oil thus procured is subsequently heated to 100° C. with water in a tin boiler, by which the albumen is coagulated, and with the mucilage separates as a scum. The oil is then passed through flannel, and run into square tin cases. The best oil of this variety is sold in London as *cold-drawn castor oil*. According to Ainslie castor oil is obtained in the East Indies also by decoction, and this process is likewise pursued in the West Indies.

The process of Figuier is now followed on the Continent of Europe on a considerable scale. It consists in mixing the seeds, first deprived of their outer coating and bruised into a paste, with alcohol. This mixture is inclosed in canvas bags, and submitted to pressure. Part of the alcohol is recovered by distillation of the mixture of oil and spirit; the residue is then mixed with a large quantity of water, when the oil rises to the surface, and is drawn off. It is again heated to remove traces of moisture, and then filtered. This process is more expensive than those previously given, and the product is inferior.

After its arrival in this country foreign castor oil is filtered, and bleached by exposure to solar light on the tops of warehouses. Of the several varieties met with in commerce, the East Indian castor oil is the most abundant. It is an oil, in every respect, of good quality, but inferior to English cold-drawn oil. American oil rarely finds its way into this country. It has a less acrid taste than the East Indian variety, but is objected to because at a low temperature it congeals quickly, deposits margarin, and becomes opaque.

When very pure, castor oil is a thickish viscid fluid of a bright yellow hue, with a slightly nauseous smell, and a mild, somewhat sweetish taste, succeeded by a slight sense of acrimony. The oil of commerce is, however, frequently of a greenish, and occasionally of a brownish colour, with a hot acrid taste. Its specific gravity is 0·9699 at 12° C.; and 0·9575 at 24° C.; it is, consequently, heavier than most other fixed oils. Its composition and properties are essentially different from those of other oils. It is distinguished from other oils by its being easily soluble in absolute alcohol in all proportions. Spirit of wine, of specific gravity 0·8425, dissolves about three-fifths of its weight. It is also readily soluble in ether. This oil forms the connecting link between the siccative and non-drying oils. By long exposure to the air it becomes rancid, and gradually hardens without becoming opaque. It retains its fluidity even at a temperature of 15° C. At a lower degree it congeals into a transparent yellowish mass. The action of heat upon castor oil has been particularly investigated by Bussy and Lecanu. When heated in a retort, so as to distil over about one-third, there remains a substance, solid at ordinary temperatures, having the appearance of a yellowish porous body resembling caoutchouc. It requires a high temperature for its decomposition, and is easily inflammable, without undergoing fusion. It is insoluble in water, alcohol, ether, and in the fixed and volatile oils. When saponified it yields a species of soluble soap, from which mineral acids separate ricinoleic acid, $C_{19}H_{36}O_3$, and some other acids. The products of distillation are a little gas, and a liquid containing acetic, *ricinic*, *ricinoleic*, and *margaritic* acids, and an odorous, colourless, volatile oil, which crystallizes on cooling.

Cotton-seed Oil.—The seeds of the cotton plant —*Gossypium barbadense*—yield an oil which is now becoming an article of commerce. Owing to the enormous quantity of cotton annually produced there must always be an abundance of seed, which it is desirable to convert to some useful purpose. Of late years this oil has attracted a greater share of attention, and means have been devised of purifying it, and removing the dark colour which it possesses in the raw state. Even now, however, large quantities of cotton-seed are annually destroyed.

Croton Oil.—This acrid oil is extracted from the seeds of the *Croton tiglium*, and is imported from Madras and Bombay. In size and shape these seeds much resemble castor-seeds. They have no smell; their taste is at first mild and oleaginous, afterwards hot and acrid.

Croton oil is extracted by expression from its seeds. The crushed seeds are submitted to the press, and the oil that flows out is allowed to stand from twelve to fifteen days to deposit; it is then drawn off and filtered. The expressed cake is treated with twice its weight of rectified spirit, and heated in the salt-water bath. The alcohol dissolves a large quantity of the oil remaining in the *marc*, and is separated from it by evaporation. Sometimes the seeds, freed from their husks, are pulverized and treated at once with spirit; the mixture is heated in the salt-water bath, allowed to cool, inclosed in a bag, and pressed. The alcohol is afterwards removed from the oil by distillation. Croton oil is of a brownish-yellow colour, has a very disagreeable characteristic odour, and a strongly acrid taste. It is soluble in alcohol and in ether. In doses of one drop it operates on man as a violent purgative. It appears to consist of a mixture of this oil with another

very acrid substance, very soluble in cold alcohol. *crotonol* ($C_9H_{14}O_2$), which irritates and reddens the skin.

Hemp-seed Oil.—This oil is extracted from the seeds of common hemp—*Cannabis sativa*. The plant grows wild in Persia, Caucasus, and the north of India. It is cultivated in various other countries. The seeds are small, ash-coloured, shining, nut-like bodies.

The oil is extracted principally in Russia. The yield is stated by Pereira to amount to 25 per cent. of the seeds. This, however, is only in extreme cases, the quantity usually obtained rarely exceeding from 15 to 20 per cent. The oil has a greenish-yellow tinge, a disagreeable smell, and a mawkish taste. It is readily soluble in boiling alcohol, and in about 30 parts of this spirit when cold. It is used in painting and in the preparation of a soft soap. It is occasionally employed in Russia as a source of light, but is apt to form a viscid adherent varnish, which impedes its passage through the lamp.

Linseed Oil.—This, the most important of the drying oils, is obtained by expression from the seeds of the common flax, *Linum usitatissimum*. This plant is extensively cultivated in this as well as other European countries, both for its fibre, used in producing thread, and for the oil obtained from its seeds. It is said to be a native of Britain; but was not cultivated till about 1533, when it was directed to be sown for the production of flax for the manufacture of fishing nets. The seeds, commonly termed lintseed or linseed, are small, oblong, smooth, and pointed at one extremity. Externally they are of a glossy brown colour, and internally yellowish white. Their taste is oily and mucilaginous. The mucilage, however, for the most part exists in the seed coats, and not in the nucleus, the latter being the richest in oil. The following analysis of linseed is by Meyer:—

	Per Cent.
Fat oil,	11·265
Wax,	0·146
Acrid soft resin,	2·488
Resinous colouring matter,	0·550
Yellow extractive and tannin,	1·917
Sweet extractive, malic acid, and salts,	10·884
Gum,	6·154
Nitrogenous mucilage, acetic acid, and salts,	15·120
Starch, with salts,	1·480
Albumen,	2·782
Gluten,	2·932
Husk,	44·382
	100·000

According to Gmelin, the ashes contain oxide of copper. The proportion of fat oil contained in the seed is certainly much greater than that given in the preceding analysis, for by expression in the cold the yield of oil is from 21 to 22 per cent. of the seeds, and by the assistance of heat, combined with a more powerful and long-continued pressure, as much as 28 per cent. may be obtained. If a very pure oil be required the process of cold expression must be pursued; a very good oil, however, may be obtained by a steam heat not exceeding 200° Fahr. The ordinary method of getting rid of the large quantity of mucilage is by steam heating, after which the seeds are bruised and submitted to pressure. The *marc* remaining after the expression of linseed oil is generally known as *oil cake*, and is an article of great importance to the agriculturist, being extensively employed, especially in the winter season, as food for cattle. By far the best oil cake is that from English seed. If extracted by cold expression (when it is termed *cold drawn* linseed oil), it is paler coloured, less odorous, and has less taste than that obtained by the aid of heat. In the latter case the oil is of an amber or brownish-yellow colour, and also more susceptible of rancidity than when cold drawn. The smell and taste of linseed oil is highly characteristic and peculiar to itself. Its specific gravity, according to Saussure, is 0·9395 at 12° C.; 0·931 at 25° C.; 0·9125 at 50° C.; 0·8815 at 94° C. It dissolves in 5 parts of boiling and 40 of cold alcohol, and in about one and a half times its volume of ether. Its constituents are on an average 75·17 per cent. C, 10·98 per cent. H, and 13·85 per cent. O, corresponding with the formula $C_{15}H_{28}O_2$. According to Schüler it contains palmitin. Gusserow by saponification obtained one-tenth margarate, and nine-tenths linoleate of lead. According to Sacc it consists of margarin and glyceride of linoleic acid. If cooled down to about minus 18° C. it may be kept some time without suffering any important change. After the expiration of a longer or shorter period, however, dependent upon the precise temperature, it becomes darker coloured, and deposits a portion of its solid constituent along with colouring matter; at a few degrees lower it becomes entirely converted into a concrete yellow mass. Linseed oil may be completely decolorized by the action upon it of ferrous sulphate in conjunction with sunlight. A solution of 2 lbs. of the salt in $2\frac{1}{2}$ lbs. of water is poured into a flask containing 2 lbs. of linseed oil, and the whole is submitted to sunlight for some weeks with frequent agitation. The oil becomes limpid and colourless, and may be drawn off by a siphon or otherwise.

Linseed oil is most largely used in the manufacture of paints and varnishes. It is used also in the preparation of printers' ink, in the preparation of black enamel for leather, and in the varnishing of oiled silk. In white-lead works linseed oil is bleached by sulphuric acid, and the small portion of acid always remaining in the oil after this operation has the good effect—by converting into sulphate any hydrate of lead that may be present in the white-lead with which it is ground—of preventing the production of the yellow higher oxide when the paint is exposed to the air. A method of purification especially to be recommended when the oil is to be used in the preparation of varnish, is to triturate the oil with dry sulphate of lead in sufficient quantity to form a milky mixture. After a week's exposure to light, and with frequent agitation, the mucus and albuminous matters deposit with the sulphate of lead, and leave the oil perfectly clear. The oil will then, after some time, become quite white. The pre-

cipitated matters form a compact membrane above the salt of lead, and become so hard that the supernatant clarified oil may be poured off. The lead sediment may again be used for the same purpose. Varnish so prepared is especially valuable in those cases where the presence of a salt of lead would be injurious—as, for instance, with lac colours, with sulphide of cadmium, and other pigments containing sulphur. When long kept in a bottle only half filled with it, the linseed oil becomes more thick, and does not dry as well as before. By this treatment, however, it acquires the property of comparatively ready solubility in alcohol, and is therefore added with advantage to several spirit varnishes to diminish their brittleness.

Caoutchouc of Oil is obtained from linseed oil as follows:—The oil is exposed for some time, as in the preparation of printers' ink, to a high temperature, when it becomes converted into a dark tenacious mass. If this be boiled for some hours with dilute nitric acid, it acquires a thick consistency, and becomes hard on exposure to the air, but softens again by the heat of boiling water, and again hardens to a consistency resembling that of caoutchouc, for which, indeed, it may in some instances be substituted. An imitation of kamptulicon is made with this substance combined with ground cork. This singular body is soluble in oil of turpentine, in bisulphide of carbon, and in dilute alkaline solutions; from the latter it is thrown down unaltered on the addition of an acid. Other drying oils, beside linseed, yield a similar substance, though not so abundantly.

Linseed oil is frequently adulterated with resin or colophony. This may be detected by digesting the oil with alcohol, decanting the latter, and adding acetate of lead, when the appearance of a white precipitate is indicative of this falsification.

Linseed oil is sold in four different forms. These kinds are—1. *Raw oil*, the oil in its natural state, as it comes from the seed. 2. *Refined oil*, or that which has had the mucilage and colouring matter separated from it. 3. *Boiled oil*, that is, oil which has been more or less treated with various substances termed *driers*, so that it may dry when in a thin coating more quickly than the original oil. 4. *Artists' oil*, the raw oil put into a variety of conditions as to thickness, colour, and rate of drying, to satisfy the sometimes fanciful requirements of painters.

The oils of this last class have generally more the character of curiosities than of utilities. They are usually made in very small quantities, and result from the special treatment of a few gallons of oil by the artists' colourman; sometimes exposing it to sunshine for a few weeks or months; sometimes treating it with plumbic acetate, litharge, &c.; not unfrequently the artist himself has some favourite method of preparing his own oil. The result generally is that such specially prepared oils are by no means remarkable for their drying properties. The strongest seldom dry in fifteen hours.

Refined oil, in paint-making, is employed chiefly as the vehicle in which to grind pigments of delicate colour. It is prepared by a variety of processes. The oil is allowed to settle in large tanks for several weeks or months, and is then treated sometimes hot, sometimes cold, with plumbic acetate or plumbic oxide, the lead being afterwards by some makers separated by sulphuric acid (see Liebig's process described above). In other cases the oil is warmed with zinc sulphate, alum, magnesia, &c., or is bleached by chlorine or some chlorine compound. In whichever way prepared, refined oil, as found in commerce, is defective in its drying properties; and hence, to quicken the work of the operative painter, arises the necessity for using, along with both raw oil and refined oil, spirits of turpentine and the compositions known as driers. Could the raw, or still better, the refined oil be made of themselves to dry with sufficient rapidity, there would be no need for turpentine, for driers, or for boiled oil (see Purification of Oil, *ante*).

Boiled Oil.—The choice of linseed oil is of peculiar consequence to the oil-boiler and varnish-maker, as upon its quality depends to a great extent the beauty and durability of the paints mixed with it. Oil expressed from unripe seed always abounds in water, mucilage, pulpy matter, and is more or less acid. Bad oil is opaque, turbid, and thick; its taste is acid and bitter upon the tongue, and it smells rancid and strong. Such oil should be separately boiled, with extra driers, and should be left to settle in a tank by itself.

Oil from fine full-grown ripe seed is limpid, pale in colour, and brilliant, *i.e.*, though it may not be perfectly bright, from not having been tanked for a sufficient time to allow the mucilage to settle completely, it has, nevertheless, a high refractive power; it is mellow and sweet to the taste, has very little smell, is specifically lighter than impure oil, and, when clarified, dries quickly and firmly.

The chemistry of the changes induced in linseed oil by its mere exposure to air are generally summarized in the statement that the oil dries—that is, that it passes from a fluid to a solid state merely by its absorption of oxygen from the atmosphere; hence it was that to aid it in drying, it was conceived to be only necessary to heat it along with certain metallic oxides, which, previously to its exposure to the air, should give it oxygen, and thereby shorten the time needed afterwards for a more complete absorption. Hence the theory of the utility of the addition to the heated oil of litharge (plumbic oxide); and hence, more recently, the superaddition, that of red lead, and subsequently (originating with Chevreul) of anhydrous binoxide of manganese.

This view is borne out by the following experiment—2500 grams. of raw linseed oil boiled for ten minutes with 30 grams. of litharge and 30 of minium, then cooled in a close vessel and weighed at the end of twenty-four hours, lose only 60 grams. in weight. (Had air been blown into the oil it would have increased 2 to 3 per cent. in weight). This loss is so small that it goes to prove that boiled oil is a simple isomeric modification of the raw oil. Linseed oil thus treated was applied to a deal board; in

twenty-four hours it was transformed into a fine transparent varnish.

To further prove that the resinification is due to absorption of oxygen, thin layers of the oil were laid upon plates of zinc, and it was found that an increase of weight took place during the resinification equal to about half the weight of the oil used.

The oldest practice of making boiled oil was merely to heat or "boil" the oil; then followed the conjoint employment of litharge; both these methods being purely empirical, being founded on practical experience alone. But the more recent processes of superadding red lead (triplumbic tetroxide) or binoxide of manganese, were, as stated above, founded on the principle of giving to the oil at a high temperature the proportion of oxygen needed to initiate its drying.

Along with these later practices there has, still more recently, crept in the conjoint employment with the lead oxides of plumbic acetate, zinc sulphate, &c. *Umber* is occasionally added, but serves only to increase the colour of the oil.

Linseed oil is boiled for two reasons; firstly, to facilitate its drying when spread in thin surfaces, either alone or mixed with paint; secondly, that it may serve as a vehicle for the mechanical suspension of the finely divided particles constituting a paint, enabling them to adhere to the surfaces on which they are spread. It must neither run into drops, nor must it leave the colouring matters behind; it should carry the colour evenly diffused through it over the whole surface upon which the paint is laid, that when dry they may together form a coating impermeable to gases and liquids.

Technically the union of these qualities constitutes a quick drying oil with a good body. It is frequently the case, however, that consumers require in boiled oil, besides these essential qualities, others which are in reality quite adventitious, to which either from experience of some particular sample, from the custom of their trade, or from the mode in which they have been led to believe good boiled oil can alone be made, they attach a fictitious importance. For instance, some persons cannot conceive a boiled oil is good unless it has a particular smell. But taking it for granted that this smell arises from the oil having been heated for a certain time to a given temperature (a thing by no means certain), it is obvious that two samples of oil may have that odour, whilst from the different ages of the oil previous to boiling, the quality of the seed from which they were expressed, or the driers employed, their qualities of colour, drying, and body (the only real requisites) may be entirely different. Other persons, again, confine good quality to a particular shade of colour and degree of brightness; a third party requires a particular shade of colour, body, and smell combined, &c.

The truth is, that these are circumstances independent of the proper treatment of the oil in the boiling process. The varying qualities of the linseed oil, according as it is new or old, made from green or ripe seed, from Baltic or East Indian linseed, &c., require a varied treatment to bring them to one standard of drying power and body. If these be the standards to be maintained, the others, which after all are only indications that the oil has been manufactured, are of no importance. This specially applies to the time-honoured method of oil boiling by fire. If a uniform quality of oil be employed and the same process always pursued, the colour and smell would be indications of the success of that particular process upon that particular oil; but at the present day the field from which linseed oil is obtained is much wider than it was of old; the boiler cannot always obtain the oil he prefers, and of necessity the mode of manufacture has to vary to some extent with each parcel of oil. The old process of working is as follows:—

After the oil has been allowed a sufficient time in the tanks to become bright and clear, it is run into an iron pan of sufficient size to hold the charge of oil to be boiled, leaving at least 6 inches free space for frothing up; and in large works a safety-pipe is let into the sides of the boiler, so that if intumescence proceeds too far the oil can be rapidly withdrawn from the action of the fire. When the pan is charged a fire is kindled in the furnace beneath, and so managed that the oil shall gradually but slowly increase in heat for the first two hours; it is then brought to a gentle simmer, and if there is any scum on the surface, this is skimmed off and put aside to be used in making putty, &c. The oil is allowed to remain at this temperature for about three hours, and then little by little the driers used—litharge, acetate of lead, umber, magnesia, sulphate of zinc, or whatever they may be—are thrown in, the oil being at the same time stirred from the bottom. The driers seldom exceed in quantity 5 lbs. to each ton of oil.

When the driers are all in, the oil is allowed to boil rather smartly for an hour; it is then counted finished. (Some manufacturers at this point throw in about one-eighth of its weight of black rosin, under the idea that the hardness of the dried oil will be thereby increased, but with the certainty that the profits on the boiling are much increased.) The pan is next carefully covered over to keep out the dust, while the fire is drawn and extinguished by water; the oil is then uncovered and left till the next morning, when it should be covered more or less entirely with a thin skin. This is cleared away, and the oil, which is still hot, is run off or ladled out into suitable vessels. At some of the smaller oil-works the oil is turned at once into the oil-pipes for sending out; in the larger factories it is stored in huge iron tanks for a few weeks, until the whole of the driers have settled, and the oil is as bright and clear as old port wine.

The sediment, called "foots," is used for putty, &c.

The boiling vessel is made either of copper or boiler plate, or is a cast-iron pan of greater or less capacity, according to the magnitude of the works; and this capacity may be that of 1 pipe of oil (about half a ton), or of 4 or 6 or 8 pipes. On an average the boiling pan holds 4 or 5 pipes, or about 2 tons of oil.

All oil-boilers should test the drying quality of each batch of oil. The writer has found that the most trustworthy mode of doing this is to dip a piece of well sized paper into the oil when cold, and hang it up to dry. If the oil is thoroughly well boiled, a varnished surface is produced over nearly the whole of the dipped portion of the paper. If the boiling has been imperfect, the upper part of the surface of the paper will be simply greasy, and the varnished coating will be confined to the lower part only. The drying is said to be effected when the paper no longer greases a finger touching it.

The thinner the layers of boiled oil the more quickly do they dry, and at 40° Fahr. the absorption of oxygen is one half less rapid than it is at 60° Fahr., so that oils dry more slowly in winter than in summer.

When heat is applied to the oil, the water (probably held by the mucilage) is first thrown off, and this water forms a yellow stained froth on the surface of the gradually heating oil. As the heat increases there are evolved, successively, acetic acid, acrolein, and other vapours and gases. Before the heat has fulfilled its work the temperature has risen to some 600° or 700° Fahr. Finally, the oil has suffered the changes peculiar to its partial destructive distillation, and passed from its original bright colour into a deep and permanent brown or reddish-brown; and, in the opinion of many consumers, the more intense this dark colour, the better is the boiling considered to have been accomplished.

The clear boiled oil, as usually made, always contains a considerable quantity of lead, is dark coloured and cannot be bleached; paint mixed with it is apt to darken, from its undergoing the well-known reaction with sulphuretted hydrogen. The process is moreover an eminently dangerous one; it produces an intolerable odour, and since the introduction of East India seed is by no means so certain as it was when Baltic linseed alone was used. The difference of climate and culture gives to the East India seed oil so different a character, as to require that it should be treated by a much slower process, and that much more care should be bestowed on it.

The East India seed oil is what is called "tender." The main reason that it cannot be boiled with safety in the ordinary way, is its great tendency to swell and froth up on the application of heat.

The imperfection of the process of boiling oil by fire, and the desire to avoid the use of lead salts consequent upon the introduction of zinc white as a pigment, led to active research on the part of many chemists. The first to make any real advance was E. Chevreul, who in a masterly paper ("Recherches Experimentales sur la Peinture à l'Huile," Mem. Acad. Sciences, t. xxii., 1850) demonstrated that by heating oil with binoxide of manganese for eight hours, at the temperature of 70° C., it was rendered sufficiently a drying oil to be used as boiled oil. C. Binks, Baruel, and Jean followed up the subject; as did also C. W. Vincent, with special reference to varnish for making printers' ink. After many discouragements, a process for oil boiling by means of steam was fairly set going, and has of late years become very extensively used.

One of the great difficulties the steam process had to contend with was that the colour of the oil is but slightly altered; and until means were adopted to secure to the oil the much-desired red-brown colour, it had no chance of success. One of the advantages of the process is hereby much diminished, since oil-boilers are compelled to adopt expedients to give a colour to the oil which otherwise it would not have. And to the practical end, an aim has to be added which frets and annoys common-sense and honesty of purpose—viz., that in addition to that of good and improved methods of manufacture, there must be sufficient similarity in appearance to accustomed samples to avoid awakening prejudices. This is the more to be deplored since the colour is obtained by the introduction of those very salts of lead which the process was devised to cast out.

According to Chevreul, Liebig, and others, linseed oil is solidified by absorption of oxygen; hence it follows that all substances which can be used as driers must be such as are capable of parting with oxygen to the oil; or else by dissolving in it, and being themselves oxidisable in combination, they in that way increase its absorptive power. There is also a class of driers, astringents, which act whilst mechanically suspended in the oil—as white copperas (zinc sulphate), &c. They do not themselves promote the absorption of oxygen, but assist in the removal of the vegetable albumen and mucilage which the oil contains, which to a certain extent impair its drying qualities. The oil is then brought more directly in contact with the oxygen of the atmosphere, and consequently dries more rapidly.

Binoxide of manganese belongs to the first class of driers, but acts *quasi* catalytically; it parts with some of its oxygen to the oil, and thus to a certain extent becomes deoxidised; but in the act of stirring the manganese oxide is brought up to the surface, is reoxidised, and is again in a position to act upon the oil.

This necessity of reoxidation of the manganese suggested the use of blowing engines in conjunction with the oil pan; and it was immediately found that the process of boiling was greatly accelerated, and that at the same time a great body could be given to the oil at a comparatively low temperature.

Driers which operate in this manner are now very generally adopted, the effect of their use being simply this—that the oil subjected to their action conjointly with a current of air has its absorptive power for oxygen very greatly increased, and retains this power when the driers, the primary incentives to absorption, are entirely removed. The oil is completely liquid, its body is somewhat increased, but on exposure to the air it becomes in a few hours covered with a thin but tough skin.

Faraday was the first to turn this property of binoxide of manganese to practical account. He was consulted by the manager of the Queen's Printing Office, as to the possibility of hastening the drying

of printing inks, so that work might be milled (that is, compressed between zinc plates passed through closely set rollers) with less delay after printing. A fortnight was the time usually allowed for the ink to set. If the printed matter was milled sooner the ink "set off" on to the zinc plates, and if the ordinary driers were used the ink formed thick skins on the rollers of the printing machine, with many other inconveniences. Faraday's far-sighted sagacity at once decided that one solution of the difficulty would be the mechanical introduction of a substance in the ink which should be almost inert till it was exposed to the air. Binoxide of manganese fulfils this condition.

In order to get the binoxide in a sufficiently fine state of division to mix with the printing inks, he devised a washing apparatus, consisting of a series of vessels arranged one below the other, like stairs. The finely powdered manganese being placed in the topmost vessel, water is run on to it, and the manganese stirred up. The black liquor passes from vessel to vessel, depositing the coarser particles first, and the finest later. Six vessels were found enough. In the last the manganese is deposited in an impalpable powder, which when worked into the ink enables it to be used without fear of injury to the plates or formes from grit. These experiments were carried out forty years ago by the help of Stephen Leighton, of the Queen's Printing Office, Shacklewell, long before the researches of Chevreul. The ink was specially manufactured by Shackell and Edwards.

By following up this investigation for Leighton Brothers for the *Illustrated London News*, Vincent found many other substances which act in the same way (notably preparations containing manganous chloride), and was thus enabled to prepare pale boiled oils, which could be used in making varnish for coloured as well as black inks. These varnishes have been used since 1859 by some of the largest ink makers and colour printers.

When manganese compounds are used as driers, the oil need never reach the temperature at which it is carbonized, consequently it remains pale in colour; as, however, consumers of boiled oil insist on its having the reddish-brown hue to which they are accustomed, litharge, or some lead salt, has to be added. By judiciously mixing one of these substances (preferably litharge) with one of the manganese compounds, a drier is obtained, by altering the relative proportions of which the boiler can give to the oil any desired shade of colour. The larger the quantity of litharge the darker the colour of the boiled oil. A lesser amount of litharge, accompanied by a greater proportion of the manganese compound, gives as a product an oil which will dry in the same time, and has less colour.

The risk of boiling over, and causing a conflagration, was one reason for the distance at which oil-boiling establishments were formerly kept from towns; the abominable smell produced by the evaporation and partial decomposition of the oil was another. Nevertheless, it is a great inconvenience to be constantly driven further and further away from those industrial centres where the product has ultimately to be used, and this has been particularly felt in the case of the oil trade. It became, therefore, a matter of absolute necessity to find means of stopping the intensely disagreeable odours arising from oil-boiling, and to secure the premises from risk of fire. This has been arrived at in a very perfect manner, as an adjunct of the steam process.

The best form of pan for oil-boiling by steam is made of copper (an iron one will give equally good results, but on account of its conducting heat less perfectly will cause the process to occupy more time). The pan is circular in shape, with a depth about equal to its diameter, and a rounded bottom. This pan is surrounded for about three-fourths of its depth (*i.e.* to the oil level, or a little above it) with an iron jacket, between which and the body of the pan steam is admitted as the source of heat.

The jacket and pan should be able to withstand a working pressure of 40 lbs. to the square inch. The top of the pan is closed by a dome rivetted to it, and forming a part of it. This dome is furnished with a man-hole, and in the centre is provided with a stuffing-box, through which passes a solid shaft surrounded by a hollow one; each shaft bears a fan, which fans, by gearing outside the pan, are made to rotate in opposite directions, intersecting each other in so doing, and, as may be conceived, producing a most thorough admixture of any fluid and solid substances submitted to their dashing and cutting action. (Henry Pontifex & Sons are the makers.)

At one side of the top of the dome is a kind of cupola, from the top of which proceeds a three-inch pipe, which is carried down to the ash-pit below the furnace of the steam-boiler.

When at work care is taken that every joint is tight; hence all vapours arising from the oil in the pan are conveyed by the pipe from the cupola through the fire, and the acrolein, &c., are destroyed. The oil-pan being at a good distance from the furnace, and the disagreeable smell being done away with, oil-boiling can be carried on without objection on the part of either the insurance companies or the public at large, even in the most densely populated districts. Vincent states that he boiled oil and made printing ink varnish in Milford Lane, Strand, for some years, without increasing the insurance on the premises of the *Illustrated London News*, though the steam was supplied from their boilers.

At the lower part of the pan an inch-pipe from a powerful air-blower penetrates through the jacket to the interior of the pan.

The workman's first care on commencing operations is to see that all his taps are in good, efficient order, and turned the right way, after which the mode of manipulation is the following:—The oil, which is drawn from the settling tanks in which it has been stored for some weeks, or at any rate days, is run into a large tank, holding one batch for boiling (two to three tons is the usual quantity, though more may be worked), and here allowed to remain for four or five hours, according to the time taken

for boiling the previous batch; matters being so arranged that as soon as one batch is pumped up into the pans another is shot into the tank. The waste steam from the boiling-pan passes through a coil of inch and a half pipe placed in this tank, so that the oil is warmed, and the separation of mucilage, &c., at once commences. In dealing with oil from East India seed this preliminary warming almost entirely stops the intumescence in the after boiling already referred to.

By the time the pan is ready the oil has acquired a temperature of about 95° Fahr.; it is then pumped up into the pan by force pumps capable of throwing a ton 20 feet upwards in three minutes. A small safety tap on the jacket is then opened, and full pressure of steam turned on. As soon as steam issues freely from the outlet the air may be counted to be expelled, and the safety tap closed. The fans are then started.

At first little or no smell is to be perceived. If the manhole be open an observer can watch the oil churning round with but little frothing, although the blades of the two fans, rotating in opposite directions, cause such a perfect commingling of the oil and the air which is in the upper part of the pan, that, looking in upon the whole fluid mass, it seems as if the bulk were greatly increased, and it goes on swelling and chafing with a hollow rumbling noise until true frothing commences.

On first turning on the steam the pressure on the boiler is rapidly reduced by the rapid condensation; but as the oil gets hotter, so does the steam pressure recover itself. The oil now begins to emit a faint sickly odour, something like that of raw oil, but intensified. It is now nearly hot enough for the air to be turned on. This may be done as soon as the steam reaches the pressure on the jacket of 35 lbs. to the square inch.

Immediately the appearance of the oil changes; its bulk appears to be still more increased; a foaming, seething vortex presents itself; the colour changes from the dark brown to a pale yellow, and a strong pungent odour, like a thousand onions concentrated, which universally accompanies the boiling of oil, makes itself known and felt by both eyes and nose, if the workman does not take the hint that it is time to close the manhole.

It may be here observed, that before the air was turned on a taper would burn in any part of the space above the oil, when it was safe from being extinguished by splashes. After the air has been blown through the oil for a short time, if both the fans and the air-pump be stopped, so that a perfectly quiescent atmosphere remains above the oil, it is found to be perfectly incapable of supporting combustion. Vincent states that even a brown paper torch dipped in turpentine is, under these circumstances, immediately extinguished.

If a dark boiled oil is required, the driers should be put in as soon as the oil is thoroughly heated throughout its bulk, which is commonly about half an hour after the steam has an indicated pressure of 35 lbs. to the square inch.

The driers have been previously ground with oil to the consistence of treacle. They are now mixed with oil, and are introduced through a funnel, with a stop-cock intervening between it and the pan, in a thin stream. It is important to secure as perfect a distribution of the driers through the oil as possible from the first, as if they are suffered to come together they coagulate, form lumps, and do not do half their work.

The quantity of driers used need not exceed three-quarters of a pound per cwt. of oil, so that there is an obvious necessity to take great pains to secure and maintain as great a diffusion through the liquid as can be achieved, and thus coincide with the new theory of oil-boiling, which requires that each particle of oil should be in contact with a particle of the drier used, and also with oxygen at the same time.

Subsequent to the introduction of the driers no attention is required, save to see that the air-pump and fan are kept constantly at work, and that the pressure of steam on the pan does not sink below 30 lbs., 35 lbs. being that which should be adhered to.

The exact quantity of air which ought to be injected for the oxidation of a given quantity of oil has not been ascertained. In practice it is found that some oils require and will consume a much larger quantity than others. The custom is to throw in as much air as the oil will take up without frothing up into the dome or the cupola, and priming over into the vapour pipe.

The cooling effect of the air thus introduced is much less than might at first be supposed. In point of fact, the pressure to which the air is subjected in overcoming the weight of the oil, lifting the heavy valves, and its friction against the tubes it passes through, considerably raises its temperature before it enters the pan. It is generally found to be raised some 20° or 30° Fahr. by the time it reaches the oil. Indeed, the pipes which it traverses frequently become too hot to be held by the hand with a firm grip.

In four hours after putting in the driers the oil is finished, and may be removed from the pan to a tank, where it remains for a week or more for the major part of the driers to settle out. When bright, it is either pumped or run off into other tanks for warehousing, or may be allowed to remain where it is for future use if there are plenty of working tanks.

The settling tanks should be lofty in proportion to the width and length. They should have two or three exit taps for the oil, the lowest being at least 4 inches above the bottom of the tank. As the oil settles slowly, the upper part is sometimes bright and clear several days before the lower half is fit to use. Underneath the tanks should be a large cock in the lowest corner, to remove the foots and sediment.

The mode of emptying the boiling pan is by allowing the oil to rush out through a two-inch tap in the centre of the bottom into pipes, which are connected by running joints, and lead it in any desired direction.

Sometimes a little difficulty occurs in dropping

the oil, owing to the orifice of the tap leading into the pan becoming stopped up by an accumulation of the old skins of oil which have fallen from the sides of the pan. This may be greatly avoided by causing the air from the blower to enter the pan through the bottom tap, and putting a second tap beyond the air inlet as an outlet for the oil. The pressure from the air-pump will then suffice to remove any ordinary obstruction. Of course, care must be taken to shut off the air and see all taps properly arranged before the oil is dropped. The workman should have a written list, and see to each one individually before starting the oil.

The action of the air alone does nothing towards making the oil a drying one. Vincent states that he has boiled oil for three consecutive days, passing in air and keeping up a high temperature during the whole time, and the resultant boiled oil has taken precisely the same time to dry as the raw oil from which it was taken. The body of the oil had, however, so much increased, that its consistency was more that of a varnish than of an oil.

If oil be subjected to steam heat alone for the same space of time, without any air except such as comes in contact with its surface, Vincent states that the consistency does not increase as in the former case; the oil simply becomes more greasy, has less difficulty in penetrating capillary tubes (as, for instance, those of paper, plaster, &c.) than it previously had, and has decidedly less drying power. In this matter he is at variance with Chevreul, who has found that the drying power is considerably hastened by simply heating the oil. It is, however, probable that Chevreul's oil was small in quantity, and perhaps had not previously settled; in this case its drying powers would be, by simply heating, "very sensibly augmented," as Chevreul puts it. The writer's experience of many hundred samples, taken at different stages of heating oil without driers, but with and without injected air, is that, as far as drying goes, the oil is not at all altered.

The advantages of the steam process of oil-boiling are very great. The close apparatus in which the work is performed secures the manufacturer alike from annoying his neighbours and injuring his own men. There is no danger from fire. The air and heat secure a sufficient body to the oil. The lead salts secure any desired shade of colour. And the drying powers can be brought into strict accordance with the old standard, viz., on wood, six hours in summer and eight in winter. The mechanical appliances reduce the time of the operation to about one-third of that which in former days was thought essential. In the ordinary working day of twelve hours, starting with cold oil and a cold boiler, two batches can be boiled without undue driving of men or machinery.

Before leaving this part of the subject, it may be as well to note that plumbic acetates must never be used with a copper pan or with copper stirrers. So soon as the oil got hot the whole of the lead would be reduced wherever it touched the oil and copper, and the oil would become the colour of ink. When an iron pan and iron stirrers are used, the reduction does not take place.

When boiled oil is for export, Vincent advises the addition of a small quantity of well settled raw oil to each barrel or drum of boiled oil, particularly if the oil has to go south. He states that long experience has shown that the oil becomes brighter after a month's voyage than it was when first shipped, and that the risk of becoming stiff in working is thereby avoided. For a three months' voyage as much as 1 gallon of well-settled raw linseed oil may be added to each 4 gallons of boiled oil with most beneficial results.

Binks describes his process as thus carried out under his own direction:—A large wooden and lead-lined vat, holding several tons of oil, is furnished with a false bottom or compartment, through which steam is passed to warm the oil, and with a contrivance for passing into the oil a large volume of atmospheric air, sent into it by a double-action air pump, capable of being thrown into and out of action at pleasure.

The oil, treated in very large quantity at a time, is mixed with hydrated protoxide of manganese, or materials yielding that substance, in quantity ranging between 5 and 14 lbs. to the ton, and the oil warmed up to 100° to 150° Fahr.

In a very short time (ten or twenty minutes, Binks states) the oil loses its peculiar yellow colour, passing through a greenish into a brownish tint, whilst the oxide disappears, being diffused through the oil. In this state of "solution," as it is called, the oil has already had given to it, by this simple, rapid, and inexpensive operation, a very considerable amount of drying power, and is fit in this state to be applied to a multitude of purposes.

If at this stage the operation be stopped, and the oil left to cool, it will let fall a very small quantity of reddish-brown deposit, the result of a combination between the manganous oxide and the colouring matter of the oil (Binks), whilst through the oil is diffused an oleate of the oxide of manganese, giving it the brownish tinge. On exposure of the oil thus treated to air, this tinge, in the first instance, passes into deep brown, as deep as that of common boiled oil; then there follows a deposit of manganic oxide (Mn_2O_3), and the oil begins to *bleach*, and gradually as the change goes on increases in its drying power. The extent to which the bleaching can finally be carried may be to produce an oil little inferior in colour to refined linseed oil, or it may terminate in producing a fine amber coloured oil.

In Binks' opinion the hydrated protoxide of manganese is a powerful deoxidiser, and its action upon linseed oil is that of withdrawing oxygen from it. He says:—"Linseed oil in its normal state appears to exercise a certain power of resistance against external influences, that would transform it from the fluid to the solid state. It yields to these influences only after a struggle, as it were. Now the hydrated protoxide of manganese, by mere contact with the oil in very minute proportional quantities, at once breaks through this state of equilibrium or power of resistance, and the oil therefore begins at once

to dry; that is, this contact initiates the action or series of actions, or removes some obstruction against their exercise, and these then proceed with all the rapidity they are capable of.

"It is scarcely necessary to remark that this hydrated protoxide is in every respect, in its mode of application, action, and results, different from the old peroxide (dioxide). Whilst the latter is used to give oxygen to the oil, the property of the former is to *abstract* it. The protoxide is a powerful deoxidising agent."

Most oil-boilers differ with Binks. Manganous oxide is certainly a powerful deoxidiser, but it merely plays the part of a "carrier;" it is oxidised by the stream of air pumped into the oil, and is itself deoxidised by the oil, and is again ready to take up fresh oxygen from the air.

Manganous oxide is so strong an absorber of oxygen that it requires the utmost care to obtain it and preserve it without its passing into a higher state of oxidation (Mn_2O_3). For the purposes of oil boiling it is therefore preferable to operate with a manganous salt, to convert this into the protoxide shortly before using, and keep it *under oil* until it is required. Manganous salts are decomposed by the alkalies, the alkaline earths, &c., but with regard to the end in view the best reagent is litharge (plumbic oxide); the plumbic sulphate formed settles very readily from the oil, and itself constitutes a good drier.

If manganous oxide is used alone the addition of 2½ lbs. to the ton of oil gives a boiled oil which dries in fifteen hours, 5 lbs. produce an oil drying in twelve hours, and 10 lbs. an oil which dries in ten hours.

The relative effects produced by mixture of plumbic oxide and manganous sulphate are shown in the following table:—

		Ton of Oil.	Drying Rate.
1.	Litharge, ...	5 lbs.	12 hours.
	Manganous sulphate, ...	2½ "	
2.	Litharge, ...	10 "	10 hours.
	Manganous sulphate, ...	5 "	
3.	Litharge, ...	14 "	7 hours.
	Manganous sulphate, ...	7 "	

The colour of the first oil is that of ordinary pale linseed. The second proportions give an oil somewhat darker, and the last yields an oil of a fine amber colour. To meet the wants of the trade a certain amount of litharge is ground up with these driers just before using, in order to increase the colour of the oil.

It has to be borne in mind that dark coloured boiled oils do not of necessity injure the colour of the white pigments with which they are mixed. Oil is bleached by exposure to air and light, and the same thing takes place with many of the coloured boiled oils. It is well known to painters, that although boiled oil of a dark colour, when applied to white paint, may when first laid on appear to have injured the colour; nevertheless, the paint will in the course of a day or two be found whiter than that made with the ordinary oil which has not been boiled. This is owing to the chemical change which it has undergone.

To make the manganous oxide with the above mixture, the following process is commonly pursued. The amount of manganous sulphate determined upon is dissolved in boiling water, and is poured upon twice its weight of powdered litharge previously placed in a tub. Two men with wooden paddles proceed to stir the two together till it forms a pasty mass; a great deal of heat is evolved, and the mixture becomes almost solid. A small quantity of raw linseed oil, just enough to keep the whole in a pasty condition, is then added, and the stirring continued; oil from time to time being added until the reaction is complete. The whole is then covered with raw oil.

When required for use the amount of driers required is measured out and ground to a fine paste, with the extra litharge added to give colour.

Acrolein (C_3H_4O).—When the volatile products arising from the destructive distillation of oils or fats are passed through a series of bottles half filled with water, the second and third bottles retain the greater portion of the acrolein, partly in solution in the water, and partly in the form of an oil floating on the surface of the liquid. When this floating oil is agitated with twenty times its bulk of water, the greater part of it is dissolved; and when this solution is distilled in a water bath, an oily matter—nearly pure acrolein—passes over at about 52° C.

According to Redtenbacher, it is most readily obtained in a state of purity by distilling, in a capacious retort, a mixture of glycerin with anhydrous phosphoric acid, or acid sulphate of potassium; the acrolein is condensed in a receiver placed in a freezing mixture. The receiver is luted on to the retort, and is provided with a tube conducting into a chimney with a good draught, so as to carry off any uncondensed acrolein. To exclude atmospheric air, the oxygen of which rapidly combines with acrolein, the whole apparatus must be charged with carbonic acid, and the current be continued to the end of the process. The distillate separates into two layers, of which the upper one consists of acrolein, and the lower one of an aqueous solution of the same substance, and containing also another body resulting from the oxidation of acrolein. The latter is acrylic acid, very analogous to acetic acid, and is produced during the distillation, even in the presence of carbonic acid. The distillate, with the addition of a quantity of powdered litharge, to retain acrylic acid, is rectified by the heat of a water bath, and the acrolein thus obtained is submitted to another rectification from chloride of calcium, and is then as pure as it has yet been obtained. Heubner and Geuther distil 1 part of glycerin with 2 parts of acid sulphate of potassium, in a flask whose bottom is protected by wire gauze. The receiver contains plumbic oxide to neutralize the acid products. The distillate is purified as above.

Acrolein is especially remarkable for the peculiarly pungent and acrid nature of its vapour, intensely disagreeable and irritating to the eyes and nose, the evaporation of even a few drops in a large room causing

a copious flow of tears in the eyes of all present, and with severe pain. Acrolein is colourless, has a high refracting index, is lighter than water, and boils at 52·4°. It burns readily with a clear bright flame. It dissolves in about 40 parts of water, and very readily in ether. When long kept it changes spontaneously into a white, flocculent, inodorous substance, which Redtenbacher named *disacryl*. The latter body is insoluble in ether, oils, acids, and alkalies. As it is formed even when acrolein is excluded from air, it is in all probability an isomeric modification of this body. According to C. W. Vincent, acrolein and its aqueous solution undergoes the same change when treated with turpentine. Sometimes acrolein by long keeping becomes transformed into a resinoid mass, which fuses at 100° C., and forms a brittle transparent mass on cooling. This substance is insoluble in water, but soluble in alcohol and in solutions of the alkalies. Acrolein owes its formation solely to the decomposition of glycerin, and its production is therefore an extremely sensitive test of the presence of the latter body. Acrolein is also produced by the action of platinum black on allyl alcohol, being, in truth, an aldehyde of the allyl series (Cahours and Hofmann).

Poppy Oil.—*Huile d'œilette, huile de pavot.*—The seeds of the poppy—*Papaver somniferum*—yield this oil by expression. This plant appears to grow wild in some parts of Great Britain. It is extensively cultivated in Hindostan, Persia, Asia Minor, and Egypt, on account of the opium obtained from it. In Europe the poppy is cultivated for the capsules or *poppy heads*, either as medicinal agents or for the oil obtained from their seeds. No analysis of the seeds appears to have been made. Poppy oil is whitish-yellow, inodorous, with an agreeable almond flavour; it much resembles olive oil; it has no narcotic properties. When pure it is much less viscous than most oils, and remains liquid even to 0° C. Its specific gravity is 0·9249 at 15° C. It is soluble in about 25 parts of cold and 6 of boiling alcohol, and in ether in all proportions. It is used as a means of detecting the presence of spirit of turpentine in essential oil. In France and on the Continent it is frequently used for culinary purposes, as a substitute for olive oil. When its drying properties are increased by treatment with litharge, it is frequently used in painting. It is employed also for illuminating purposes.

Walnut Oil.—This drying oil is derived from the kernels of the *Juglans regia*, or walnuts. The nuts are freed from their ligneous shells, inclosed in bags, and submitted either to cold or hot pressure. That prepared by hot pressure has a peculiar taste and smell, the latter being especially recognizable during its combustion. The oil obtained by cold expression is pale, yellowish-green, or almost colourless; has an agreeable odour and taste, and a sirupy consistency. If coloured it loses the greenish hue after some time. The nuts yield about 50 per cent. of oil. Walnut oil congeals at about the same temperature as linseed oil, and possesses the property of drying by exposure in even a higher degree than the latter. In drying it absorbs $15\frac{1}{2}$ times its volume of oxygen, at the same time giving off carbonic acid to the amount of two-fifteenths of the oxygen absorbed. The hot-pressed oil is usually high coloured, has a powerful odour, and contains large quantities of mucilage. The specific gravity of walnut oil, according to Saussure, is 0·9283 at 12° C.; 0·9194 at 25° C.; and 0·874 at 94° C.

It is principally used in painting and by varnishers, and being comparatively clear and colourless is especially valuable as the vehicle for flake white and other pigments, when it is desired to preserve the brilliancy of their tints.

Animal Fats. See also Candle.

Lard Oil.—This fluid oil is prepared from lard in the same manner as is directed for tallow oil. It is considered much superior to sperm or olive oil for greasing wool, and from its low price is largely used. It is usually sufficiently white and clear for use, and should on no account be bleached by chemical means, as it is liable to retain enough of the bleaching agent to injure its quality, and render it inapplicable for many purposes.

Neat's-foot Oil.—This oil is obtained from the feet of oxen; and as it remains liquid below 32° Fahr., and is in other respects a useful lubricant, is much employed to oil machinery. The feet, as collected from the slaughter-houses, are soaked in cold water to remove the blood, and after removing the sinews, are placed perpendicularly in sufficient boiling water to cover the hoofs. In about a quarter of an hour they are to be taken out, and the hoof separated by a suitable machine. The next step is to joint them with a knife, to sever the toes from the large bone. The latter is boiled with water by steam, while the former, which are more obstinate in yielding their fat, are boiled in the open pan with water previously used for the large bones. After the boiling, the liquid is left to repose, so that the oil may rise to the surface and be drawn off. The collected oil deposits after some time a thick stratum of dirty semifluid fat, from which the clear supernatant portion must be decanted.

This oil consists of olein, margarin, and stearin. It is very frequently adulterated with horse oil, common lard oil, bone fat, some vegetable oils, and even with fish oils. The pure oil is not liable to change or rancidity, and is used as a lubricant; and is especially useful for machinery exposed in cold situations, as in the case of church clocks, &c., which require an oil not liable to become concrete.

Tallow Oil.—The liquid fat separated from tallow by pressure is known under this name. The best method of obtaining it consists in steaming the tallow in wooden tubs for several hours, drawing off the upper clear portion after sufficient repose for subsidence of foreign matters, and gradually cooling in large tubs between 70° and 80° Fahr. These tubs are provided with a cullendered diaphragm, about 6 inches from the bottom, and which should be covered with coarse flannel cloth. During repose the solid portion of the tallow separates in granules from the

superstratum of fluid olein, and deposits upon the diaphragm, thus allowing the liquid olein to percolate upon the opening of the cock at the bottom, and be drawn off into receivers. The solid residue, upon being subjected to pressure in Russian canvas bags, yields more olein, and itself remains hard and white. Tallow oil is thick and mushy, and admirably suited to the manufacture of the finer kinds of soap.

Fish Oils.—Certain fish, especially the *Cetacea*, yield a greasy fluid or oil, called or named according to the fish whence it is extracted. All fish oils contain certain peculiar animal matters which impair their illuminating power, but do not injure them for the purposes of the soapmaker. They are extracted by melting the blubber, and the foreign matters are then partially separated by steaming the oil and allowing it to repose. Under the term *train oil*, are included whale, seal, cod, shark, and all oils obtained from fish of a like nature.

Cod-liver Oil.—This oil is extracted from the liver of the common cod, and various other allied speciesof fish, but principally from the above (*Gadus morrhua*) and the ling (*Lota molva*). The method pursued in Newfoundland for its extraction is as follows:—The work people take a half-tub, and, boring a hole through the bottom, press hard down into it a layer of spruce boughs, upon which they place the livers, and expose the whole apparatus in as sunny a place as possible. As the livers corrupt, the oil runs from them, and straining itself through the spruce boughs, is caught in a vessel set under the hole in the tub's bottom. According to Dr. De Jongh, the usual mode of preparation in Norway is to store the livers in vats or tubs as soon as they are separated from the fish, where they are left until the end of the fishing season, when the oil that has separated is decanted, and forms the pale oil of commerce. The residue of the livers, being then submitted to heat, yields the darker oil.

The best English oil, according to Dr. Garrod, is thus prepared:—The livers are collected daily, so that no trace of decomposition may have occurred, carefully examined, in order to remove all traces of blood and impurity, and to separate any inferior livers; they are then sliced and exposed to a temperature not exceeding 180° Fahr., until all the oil has drained from them. This is filtered; afterwards exposed to a temperature of about 50° Fahr. in order to congeal the bulk of the margarin, and again filtered and put into bottles well secured from the action of the air.

In the ordinary mode of manufacture every liver is opened, examined, washed free from blood, and if sound and fit for use is cut in pieces, and put with others into a large jacketed pan with a portion of water. To the external surface of this pan steam is admitted, and the temperature being very carefully adjusted to about 180° Fahr., the livers are heated for a sufficient length of time to allow of a complete separation of the oil. The result of this process is the production of a sweet and nearly colourless oil, which is skimmed off and filtered through flannel. This, having been congealed for the separation of its margarin, is again filtered when required for use.

Three varieties of cod-liver oil are met with in the English market, and are known as the pale, the light-brown, and the dark-brown or black. The first is that extracted from the livers before putrefaction has commenced; the two latter have either remained longer in contact with the livers, have been prepared at high temperatures, or have been obtained from livers in a state of decomposition.

Porpoise Oil.—This, the produce of the *Delphinus phocæna*, much resembles whale oil. It is liquid, and has a yellow colour. When freshly extracted it has a fishy smell, but by exposure to sun and air becomes nearly inodorous. It then, however, acquires an acid reaction. It is soluble in about 5 parts of boiling absolute alcohol, but a portion of its solid constituent is deposited on cooling. By saponification it yields glycerin, with oleic, margaric, and phocenic acids.

Seal Oil.—The seal fishery is by far the most important part of the trade of Newfoundland, the annual catch of the fish being little short of three quarters of a million. The principal seals captured are the *hood* and *harp* seal, of which the latter is the best and most productive. The first operation after landing and weighing is the skinning, or separation of the fat from the skin; after which the fat is cut off, and transferred to the seal-vat. The latter consists of what are termed the *crib* and the *pan*. The crib is a strong wooden erection, from 20 to 30 feet square, and 20 to 25 in height. It is firmly secured with iron clamps, and the interstices between the upright posts are filled in with small round poles. The floor is of strong timber, capable of sustaining 300 or 400 tons. The crib stands in a strong wooden pan, 3 or 4 feet larger than the square of the crib, so as to catch all the droppings. The pan is about 3 feet deep, and tightly caulked. A small quantity of water is kept on the bottom of the pan, for the double purpose of saving the oil in case of a leak, and for purifying it from the blood, and any other foreign matter of a higher density. The oil extracted by this process is all cold-drawn, which accounts for the disagreeable odour of seal oil. When the vats begin to run the oil drops from the crib upon the water in the pan, and as it accumulates it is drawn off into casks, and is ready for exportation. The first running, which is caused by compression from its own weight, continues from two to three months, yielding what is termed *pale* seal oil, until from 50 to 70 per cent. is drawn off, according to the season, and also in proportion to the quantity of old seal fat put into the vat. Owing to its toughness the latter does not yield to compression, nor does it give up its oil until decomposition sets in; and hence it does not, by this process, yield pale seal oil. As putrefaction proceeds the colour changes to straw; and as the season advances becomes every day darker, and a more nauseous odour is given off, until the brown oil at last runs out. As this running slackens, it becomes necessary to turn over what remains in the vats. The crib being generally divided into nine apartments, or *pounds*, this operation is performed by first emptying one of these, and dispersing the contents

over the others; and then by filling and emptying them alternately, the entire residue—a complete mass of putrefaction—is turned over. By this means a further quantity of brown oil is obtained. The remains are then finally boiled in large iron pots, which during the whole season are in constant requisition for boiling the cuttings and clippings of the skin, and other parts of the pelts, which it is unadvisable to put into the vats. The produce of this, and the remains of the pelts, are what is termed *boiled seal oil*. The refuse from the vats is found to be very valuable manure, and is readily purchased by the farmers in the neighbourhood.

S. G. Archibald, of Newfoundland, states that the different kinds of seals' fat, if taken while fresh, and subjected to a process of artificial heat, are capable of yielding not only a uniform quality of oil, but the oil so obtained is much better in quality than the best prepared by the old process, and free from the unpleasant smell common to all seal oil. He afterwards invented a steam apparatus for *rendering* seal and other oils, which is said to answer the purpose admirably.

Seal oil is used solely for illuminating purposes, and when tolerably pure answers admirably, giving a beautiful brilliant light, and producing no offensive smell, nor any clogging of the wick. Owing to the offensiveness it communicates to its salts, it is not applicable for the production of soap.

Shark Oil.—This oil is procured from the liver of the basking shark (*Squalus maximus*), of the bay of Galway, or sun-fish, as it is commonly called. The quantity of oil obtained from a single fish frequently amounts to 120 gallons. It is light yellow, of specific gravity 0·870 to 0·876, and retains its fluidity several degrees below the freezing point of water. It is said to give a brilliant flame, and without clogging the wick. Ronalds, who made a partial examination of it, reports that it consists of glycerin, a peculiar oleic acid, very rich in carbon, and another undefined liquid oil.

Sperm Oil.—This oil is obtained from the white whale (*Physeter macrocephalus*). This, termed also the *cachalot* and sperm whale, is remarkable for the enormous size of its head, which is square, and apparently cut off in front. The animal is pursued chiefly for this oil, but it yields also *ambergris*. The oil is met with in several parts of the body, but the head is the principal receptacle of it. Here it is found in a large excavation of the upper jaw, anterior to, and quite distinct from, the true cranium which contains the brain. Like the fat of other animals, this oil is contained in cells, or cellular membrane; but besides these cells, there are also ligamentous partitions going across, which serve as supports for the enormous quantity of oil of which the bulk of the head is principally made up. Sperm oil is extracted from the *case* by means of an opening made in the triangular-shaped cavity situated in the right side of the nose and the upper surface of the head, and the liquid contents are removed by a bucket. The dense mass of cellular tissue beneath the *case* and nostril, and which is technically called *junk*, also contains oil. Directly it leaves the skull of the animal, the oil begins to deposit large quantities of *spermaceti*, in the form of small crystalline laminæ, from which the oil flows out by pressure, and is subsequently purified by the addition of a small quantity of solution of potash, which precipitates certain matters by neutralizing the acid that held them in solution. Sperm oil is of a yellow colour, has a slightly unpleasant smell, but is well suited for burning in lamps. It saponifies easily, and the soap obtained is brown, rather soft, and entirely soluble in water. See Candle.

Whale Oil.—This well-known fish oil is obtained by boiling the blubber of the *Balæna misticetus*, or great northern whale. It was formerly found on the east shores of Greenland, but of late years in Davis' Straits and the interior of Baffin's Bay. The whale fishers merely cut out the blubber, pack it into casks, and carry it to the seaports to be melted out. The carriage gives rise to an incipient decomposition of the animal matters and of the fluids attached to the blubber, which, although it aids the melting, occasions the formation of a peculiar fat, termed *phocenin*, which is the cause of the disgusting odour which always accompanies train oil. The cellular tissue of the blubber thus becomes so broken down that the oil runs off by itself, when the whole is put into casks with wirework bottoms, such as are used in the melting houses. The oil is afterwards heated to 212° Fahr., that the impurities may the more easily separate, and after standing some time the clear oil is decanted.

In train oil the impurity is not mucus, as in the vegetable oils, but animal gelatin or glue, and besides this, volatile, stinking matters. Some clarifiers use a solution of tannin for purifying it, which forms with the gelatin insoluble flakes; others employ metallic salts, as sulphate of copper or acetate of lead, which act in a similar manner. The nauseous odour is most easily removed by bleaching powder.

The colour of whale oil is brown, and it has a disagreeable fishy smell. Its specific gravity is 0·927. When cooled to 32° (0° C.) it deposits stearin, and the residual oil is soluble in less than its own weight of boiling absolute alcohol; the stearin is soluble in about twice its weight of this liquid. When the solution is cooled it deposits first white brilliant crystals, and afterwards crystals tinged with yellow, and a thick brown liquor remains.

Adulteration of Oils.—The admixture of fish oil with animal or vegetable oils may be readily detected by the brown or black hue produced by the action of a stream of chlorine, and also, according to Calvert, by the reddish coloration developed by boiling a mixture of the oil with solution of caustic soda. For the detection of a mixture of a drying with a non-drying oil, several methods may be applied, as that of Poutet, which consists in the application of mercuric nitrate, by which the non-drying oils yield elaidin; or that of Boudet, which depends upon the same reaction, to produce which, however, nitrous acid is substituted for the mercury salt; and, in addition, the reaction dis-

covered by MAUMÉNE, who showed that the non-drying oils gave rise to a much higher temperature, when mixed with strong sulphuric acid, than is the case with those belonging to the class of driers. The fixed oils which may be solidified by BOUDET'S method are those of sweet almonds, of filberts, and of colza; and of the drying oils, castor oil only is solidified by this treatment: 100 parts of the oils mentioned, when treated by a mixture of 9 parts of nitric acid with 1 of nitrous acid, require different lengths of time to become solid, as shown in the table subjoined:—

Oils.	Colour developed by addition of the mixture.	Number of minutes required for congelation.	Proportion.
Olive oil.....	Greenish-blue, ..	73	10·0
Sweet almond oil,	Dirty-white, ...	160	22·2
Oil of filberts,...	Greenish-blue,...	103	14·0
Oil of acajou,....	Lemon-yellow,..	40	6·0
Castor oil,.....	Golden-yellow,..	603	82·6
Colza oil,.....	Yellowish-brown,	2400	328·0

HEIDENREICH determines the purity of the fixed oils, and the admixture of cheaper oils, approximately, as follows:—First, by observing the peculiar smell of the oil when gently heated in a small porcelain or platinum capsule, by means of a spirit lamp. The odour evolved will resemble that of the plant or animal from which it was obtained. This characteristic is said to be valuable if observed in conjunction with the genuine oil, and to furnish accurate indications of the presence of linseed, whale, train, or rape oils in any mixture. The smell of the oil, however, as observed by PERROT, is not always a safe criterion, since an oil of the same fruit or nut has not always the same odour, but differs with the climate where produced, and the varied mode of extraction. HEIDENREICH further applies concentrated sulphuric acid, in the proportion of one or two parts per cent. of oil, and by this admixture a very intense action immediately ensues, the temperature rises, and the mixture becomes coloured. A few drops of the oil are placed on a glass plate, having a sheet of white paper underneath; and to the oil is added a small drop of sulphuric acid, of specific gravity 1·632, when, according to the oil employed, a characteristic colour will be developed without stirring. In the case of *rape oil*, a greenish-blue ring gradually forms at a certain distance from the acid; whilst towards the centre, where the action is more intense, light yellow-brown streaks may be observed. With *oil of black mustard*, the reaction much resembles that of rape oil, but is more violent. In *train oil*, a very peculiar motion occurs, commencing at the centre, and extending to the outside; at the same time a red tint appears, which grows more and more vivid, until after ten or fifteen minutes the margin assumes a violet tinge, which in about two hours is uniform throughout. *Olive oil* instantly becomes pale yellow, and afterwards yellowish green. In *poppy and sweet almond oils*, the colour developed resembles that of the greenfinch, but afterwards becomes of a dead yellow hue. In *linseed oil*, a beautiful dark brownish red web is formed, gradually changing into brownish black. Lastly, *tallow oil* is rendered brown.

If, in the process of HEIDENREICH, instead of the acid being allowed to act on the oil undisturbed, the two liquids are stirred together by means of a glass rod, the phenomena vary from those above described.

PERROT, reviewing the process of HEIDENREICH, directs twenty drops to be employed; and instead of the glass-plate and white paper, he uses capsules of white porcelain. In the place of sulphuric acid, he used also a saturated solution of bichromate of potash in this acid, and in the proportion indicated above, namely, 1 drop to 20 of oil. In applying this method, it is always necessary, to insure greater certainty, to compare the effects upon the oil to be examined, with an oil the purity of which is undoubted. The appended table shows the reactions produced by sulphuric acid alone, and by the solution of bichromate of potash in the acid:—

Oils.	Sulphuric Acid.		Solution of Bichromate of Potassa in Sulphuric Acid.
	Not Stirred.	Stirred.	
Tallow oil,.....	Reddish spots with reddish circles.	Reddish-brown.	Reddish-brown.
Sweet almond oil.....	Greenfinch yellow, with orange spots.	Dirty-green.	Yellowish small lumps.
Train oil,.....	Brown small lumps on a brown ground.	Lees of wine.	Brownish-red small lumps on a red ground.
Hemp-seed oil, ...	Reddish small lumps on a yellow ground.	Greenish-brown.	Yellow small lumps on a green ground.
Rape-seed oil,.....	Scarcely perceptible spots, or slight green coloration.	Green.	Yellow small lumps on a green ground.
Fish-liver oil,.....	Dark-red.	Dark-red.	Dark red.
Linseed oil,.....	Reddish-brown.	Clotted on a grey or green ground.	Brown small lumps on a nearly colourless or slightly green ground.
Oil of madia sativa,.....	Slightly reddish-brown, underneath a film inclining to grey.	Olive-green.	Light-brown small lumps on an olive-coloured ground.
Nut oil,.....	Yellowish-brown.	Clotted dark-brown.	Small brown lumps.
Olive oil,.....	Yellow, or orange-yellow.	Dirty-brown.	Brown.
Poppy oil, ...	Yellow, or greenish-yellow spots.	Olive or slightly green.	Small yellow lumps on a yellow or colourless ground.
Neat's foot oil,.....	Yellow slight spots.	Dirty-brown.	Brown spots on a similar ground.
Castor oil, ...	Yellow slight spots.	Almost colourless.	Slightly green.

GENERAL TABLE OF REACTIONS.

Oils.	Caustic soda, spec. gravity 1·340.	Sulphuric acid, spec. gravity 1·475.	Sulphuric acid, spec. gravity 1·530.	Sulphuric acid, spec. gravity 1·635.	Nitric acid, spec. gravity 1·180.	Nitric acid, spec. gravity 1·220.	Nitric acid, spec. gravity 1·330. + Caustic soda, spec. gravity 1·340.		Phosphoric acid, syrupy.	Sulphuric acid + nitric acid.	Aqua regia. + Caustic soda, spec. gravity 1·340.	
Olive,.....	slight yellow.	green tinge.	greenish-white.	light-green.	greenish.	greenish.	greenish.	fluid white mass.	slight green.	orange-yellow.	—	fluid white mass.
Gallipoli, ...	ditto.	ditto.	grey.	brown.	ditto.	ditto.	ditto.	fibrous white mass.	ditto.	dark-brown.	—	fibrous yellowish-white mass.
India nut,....	thick and white.	—	dirty white.	light-brown.	—	—	—	ditto.	—	orange-white.	—	fibrous white mass.
Pale rapeseed,	dirty yellowish-white.	—	pink.	brown.	—	—	—	fluid white mass.	—	dark-brown.	—	fibrous yellowish-white mass.
Poppy,.....	ditto.	—	dirty white.	—	—	yellowish-red.	red.	light-red fluid mass.	—	slight yellow.	—	fluid intense rose-colored mass.
French nut,...	ditto.	brownish.	grey.	brown.	yellow.	red.	dark red.	fibrous red mass.	brown yellow.	dark-brown.	yellow.	fibrous orange mass.
Sesame, ...	ditto.	green tinge.	greenish dirty white.	—	orange-yellow.	ditto.	ditto.	fluid red mass with brown liquor beneath.	—	green, becoming intense red.	ditto.	fluid orange mass with brown liquor beneath.
Castor,.....	white.	—	dirty white.	—	—	—	—	fibrous white mass.	—	brownish-red.	—	fibrous pale rose-colored mass.
Hempseed, ..	thick brownish-yellow.	intense green.	intense green.	intense green.	dirty green.	greenish dirty brown.	greenish dirty brown.	fibrous light brown mass.	green.	green, becoming black.	green.	fibrous light-brown mass.
Linseed,.....	fluid yellow.	green.	dirty green.	green.	yellow.	yellow.	green becoming brown.	fluid yellow mass.	brown yellow green.	ditto.	greenish-yellow.	fluid orange mass.
Lard,.....	pinkish-white.	dirty white.	dirty white.	light-brown.	—	—	very slight yellow.	fluid mass.	—	brown.	—	fluid pink mass.
Neat's-foot, ..	dirty-yellowish white.	yellow tinge.	brownish dirty white.	brown.	light-yellow.	light-yellow.	light-brown.	fibrous white mass.	—	dark-brown.	slight yellow.	fibrous brownish-yellow mass.
Sperm,.....	dark-red.	light-red.	red.	intense brown.	slight yellow.	ditto.	red.	fluid mass.	dark-red.	dark-brown.	ditto.	fluid orange yellow mass.
Seal,.....	ditto.	ditto.	ditto.	ditto.	pink.	light red.	ditto.	ditto.	ditto.	ditto.	ditto.	ditto.
Cod liver,....	ditto.	purple.	purple.	ditto.	—	—	ditto.	ditto.	ditto.	ditto.	yellow.	ditto.

TABLE FOR THE DETECTION OF THE FAT OILS.

At the ordinary temperature					After boiling		
5 vols. oil and 1 vol. caustic potash 1·34 are well shaken together. The mass is:—	Snow-white: Almond oil, good rape oil, bleached olive oil.	Yellowish: Poppy, olive, rape, sesame.	Greenish: Linseed, hemp, artificially coloured oils.	Rose: Refined rape.	Brown and solid: Hemp.	Yellowish-brown fluid: Linseed.	Red: Train oil.
Equal vols. of oil and fuming red nitric acid are carefully poured into a test glass. At point of contact a ring is formed, and this is:—	Small and bright-green, the oil itself is flocky: Almond.	Dark-green, rose coloured above: Poppy.	Broad, beautifully bright bluish-green: Olive.	Boron red: Cod-liver.	Green, red above: Linseed.	Brownish-red, greenish below: Rape.	The whole oil in time coloured red: Linseed.

10 drops of oil and 2 drops of acid.				Equal volumes of oil and acid.			
				Without carbon disulphide.			With carbon disulphide.
The oil is mixed with concentrated sulphuric acid in a test glass; the point of contact is coloured:—	Fine green, with brown streaks: Rape.	Yellow, on shaking brownish-olive-green: Poppy.	Red, passing into black streaks: Train oil.	After shaking, full dark green: Rape.	Green: Linseed, Hemp.	Red: Train.	With 12 times its volume, violet turning brown: Train.

By boiling with plumbic oxide and water a plaster is formed, the consistency of which is:—	Solid: Olive.	Greasy: Rape, almond, sesame.	Greasy, but drying after a time: Drying oils.

Solubility of oil in alcohol:—	1 : 1 Castor oil.	1 : 25 Poppy.	1 : 30 Hemp.	1 : 40 Linseed.	1 : 60 Almond.

CALVERT'S reactions are given in the table on preceding page; they consist in the employment of caustic alkali, and of various acids at different degrees of dilution, as well as mixtures of acids, and of acids and alkalies, successively applied. The first test in the list is employed in the proportion of 1 volume of solution to 5 of oil, and is especially valuable to distinguish fish from other vegetable and animal oils. The test and oil are to be well mixed, and then heated to the point of ebullition. In the case of sulphuric acid the same proportions as of caustic soda are employed in each case, and the mixture well agitated. With the acid of specific gravity 1·475, the appearance is noted after standing fifteen minutes; with that of 1·530, after reposing five minutes; and with that having the density 1·635, after two minutes. With nitric acid, the mixture is made in a like proportion in each case, and the reaction noticed after five minutes. The caustic soda and nitric acid are applied together, by adding 10 volumes of the former to 5 of the oil which has just been acted upon by one of nitric acid. The phosphoric acid is employed precisely as the other acids, and is extremely sensitive in the case of fish oils. The sulphuric and nitric acids are used in the proportion of 1 volume of a mixture of equal measures of acid with 5 of oil, and the appearance is observed after the lapse of two minutes. This test is especially applicable to the detection of oil of sesamum in admixture with other oils. Lastly, the aqua regia employed is composed of 25 volumes of hydrochloric acid, of specific gravity 1·655, and one of nitric acid, of specific gravity 1·330, and is allowed to remain at rest about five hours. The reactions given are those that ensue when a mixture of 5 volumes of oil with 1 of aqua regia is agitated, and allowed to stand five minutes. On the subsequent addition of caustic alkali to this mixture, a very vivid and distinct coloration is perceptible in many cases, and this, with the other appearances mentioned, render this last a most valuable agent for the detection of several instances of admixture.

The above table for the detection of the fat oils was arranged by G. GLÄSSNER. It gives at a glance the ordinary reactions. Adulteration with mineral oil can be detected by the fluorescent properties it imparts to all animal and vegetable oils, and by the strongly marked aromatic burning flavour it communicates to mixtures containing it.

The first-mentioned property is brought out by smearing a metallic surface, such as tin plate, with the oil, and then viewing it at different angles in the open air or sunlight. So characteristic is this that most mechanics who use oil can detect mineral oil at once, even when present in very small quantity.

When the oil is dark-coloured (for instance, a dark Gallipoli or a brown rape), it may be necessary to refine the sample by successive treatments with concentrated sulphuric acid and weak soda solution, or lime water, in the way oils are usually refined. Mineral oil can then be detected in the sample by a pale azure blue ring, about one-sixteenth of an inch deep, at the junction of the surface of the oil with the sides of the glass jar.

It is important to test for mineral oil or resin oil before proceeding to test specific gravities, because mineral oil ranging in specific gravity between 0·880 and 0·900, and resin oil being nearly 1·000, adjustments in specific gravity, resembling those of the natural oils, can be easily effected. (J. J. COLEMAN).

A method of distinguishing fatty oils, by the differences in the amount of heat produced by mixing 1 part of sulphuric acid with 3 parts of the oil to be tested, was suggested by MAUMÉNE, and

elaborated by FEHLING. There is a great variation in the amount of heat produced. Thus, with rape oil, a gain of temperature of 100° Fahr. is observed, as against 68° with olive oil.

J. J. COLEMAN objects to the colour tests that there are many oils which have not been examined, and the impurity of those treated causes many variations. He also condemns CALVERT'S processes, on the ground of liability to error from colour blindness.

GELLATLEY and COLEMAN consider the relative liability of oils to ignite a trustworthy indication. The experiment is made by imbuing a handful of cotton waste with the oil to be tested, and placing it tolerably loosely in a paper box, inclosed in a hot-air bath kept at a temperature of 200° Fahr. After a certain length of time the mass enters into active combustion:—

	Hours.	Minutes.
Boiled linseed on cotton waste,	1	15
Seal oil "	1	40
Raw linseed "	4	0
Lard oil "	4	0
Gallipoli olive "	5	0
Refined rape "	9	0
Seal oil on wool,	3	0
Whale oil "	3	15
Whale oil on cotton,	3	0
Whale oil on jute,	9	0
Olive oil on cotton,	4	0

Sperm oil is the dearest oil in the market. J. J. COLEMAN states that only 3000 tons are imported annually. As it has been found to answer better than any other vegetable or animal oil for greasing the spindles of cotton, woollen, and worsted mills, and the supply is insufficient for over a fraction of the spinning mills of the United Kingdom, it is liable to be adulterated.

In examining sperm oil he advises noting the following points:—1. To examine for mineral oil. 2. To examine the drying properties of the oil by exposing some of it in a thin layer to 200° Fahr. for some hours. 3. The other fish oils darken much more than sperm with dilute sulphuric acid. 4. The most likely adulterant is African fish oil, which produces more intense heat when mixed with concentrated sulphuric acid: thus, 1 pint of acid and 4 of sperm oil develop about 112° Fahr. of heat against 250° Fahr. with the fish oil 5. Test the viscosity. 6. The specific gravity is 0·875 to 0·882.

Tallow and lard oleins are next in value. These oils, obtained by pressure of animal fats, are practically free from tendency to gumming and clogging by absorption of oxygen. In examining these oils we have variations in quality from carelessness in manufacture, the oil being dark coloured, or having too strong an odour, or an acid reaction from slight rancidity. The variations from adulteration will be in the direction of the non-drying properties of the oil being interfered with.

The specific gravity should not exceed 0·915. If the oil is heavier it may contain fish oils, olive oils, cocoa-nut olein, or seed oils. All but the last may be detected by the smell, colour, taste, and CALVERT'S tests. The real difficulty lies with the seed oils, one of which, rape oil, is nearly of the colour, and exactly of the specific gravity of the animal oleins.

If a sample of animal olein be of too great specific gravity it probably contains some of the partially drying oils, of which the chief representative is cotton-seed oil, ranging in specific gravity between 0·920 and 0·930. American lard oil is frequently adulterated to a large extent with cotton-seed oil. The percentage can almost be calculated by the increase in the specific gravity, and the same remark applies to the other drying seed oils, with the exception of henbane seed, horse-chestnut, plum-kernel, and rape. The first three may be disregarded, so that the detection of rape oil is the chief point. The processes are:—

1. Heating the oil to 400° Fahr., and allowing it to cool to 90°. Tallow and lard oils are rendered odourless, whilst the peculiar penetrating smell of rape oil is enhanced.

2. One part by weight of the oil to be tested is mixed with 3 parts of concentrated sulphuric acid, and the heat developed is compared with that developed by a similar experiment made with pure oil.

3. The mercuric nitrate test is said to indicate the presence of over 10 per cent.

Finally, lard oil is distinguished from tallow olein by difference of viscosity.

Olive oils vary in colour from a fair yellow to a deep olive green; and in smell, from the sweet smell of salad oil to the powerful odour of the dark varieties. Their commercial value depends on their possessing non-drying qualities; but their price is likewise kept up by the fire insurance offices, who laid down the law that olive is the only oil to be used for wool-greasing unless an extra premium be paid.

Excepting the particularly fine qualities, the bulk of olive oils are the cheapest of the so-called commercial non-drying oils; adulteration with drying oils, fish oils, mineral and resin oils, only has to be guarded against.

Mineral and resin oils must be carefully looked for, because owing to the dark colour and smell of olive oils they might be easily overlooked.

The specific gravity of olive oil is 0·917. Rape oil, a cheaper oil, would make it lighter, and cotton-seed oil heavier, but a proper mixture of the two could be adjusted exactly to the specific gravity of olive.

The fish oils are to be sought for by the smell, and by CALVERT'S tests. The four practical tests in use for seed oils are:—

1. The nitrous acid or mercuric nitrate test. 2. The characteristics of the amides produced by liquid ammonia. 3. The rise of temperature produced by mixing with concentrated sulphuric acid. 4. The characteristics of the action of solution of potassium carbonate on the oil.

Rape oils are inferior to olive oils in non-drying properties, but superior to them in smell and appearance. Notwithstanding their slight tendency to gum, they are most extensively used for engine and machinery lubrication. The specific gravity

should never exceed 0·916; if it does, it is a sure indication of the presence of one or more of the following oils, viz.:—The fish oils, which are easily detected by the smell or CALVERT'S tests; or other seed oils of a more or less drying character, such as sesamum, sunflower, cress, hemp, cotton, niger, and linseed, all having a specific gravity varying between 0·920 and 0·935.

Thus, if rape oil indicates 0·918 specific gravity it points out the probable presence of over 50 per cent. of these oils, though the smell and colour might be only very slightly affected. These oils deteriorate rape by increasing its tendency to clog.

The chief adulterant is cotton-seed oil. It is easily detected.

1. It increases the specific gravity (mineral and resin oils being proved absent).

2. It raises the freezing point of rape oil, pure rape oil being perfectly liquid at 32° Fahr.

3. Test the drying property by small capsules of oil exposed to 200° Fahr.

Linseed Oil.—The specific gravity is 0·937. Mineral and resin oils must be carefully looked for. In their absence fish oils can be detected by smell, and by CALVERT'S reactions.

The most likely adulterants are cotton-seed and niger-seed oils. These may be recognized by—

1. Specific gravity. 2. Materially raising the freezing point. 3. Decreasing the drying properties.

Fish oils are not much liable to adulteration, because, as a rule, there are no oils sufficiently cheap for the purpose, except occasionally cotton seed, and perhaps linseed oil.

They may, however, be mixed with each other; some varieties, as porpoise oil, herring oil, and East Indian fish oil, being cheaper than others. The points, then, to observe, are—

1. Mineral and resin oil. 2. The drying properties of the sample. 3. The viscosity.

OILS, ESSENTIAL. See PERFUMERY.

OPIUM.— English, French, German, and Latin. The dried juice of the head of the poppy—*Papaver somniferum.* The word is derived from the Arabic *afioum.* The poppy is very extensively cultivated in Asiatic Turkey, Egypt, Persia, India, and occasionally in France, Germany, and England.

History.—Opium, under the name of Μηκώνιον, is mentioned by THEOPHRASTUS (3 B.C.). SCRIBONIUS LARGUS (A.D. 40) ascertained that the pure drug was the produce of the capsules, and not of the foliage of the poppy plant. DIOSCORIDES (A.D. 77) showed that ὀπός, the juice of the capsules, far exceeded in strength μηκώνειον, the preparation made from the whole of the poppy plant. He also described the mode of incision, and states that adulteration, with the sap of *Glaucium*, *Lactuca*, and gum, was practised. PLINY describes *Opion*, and shows its use in medicine. (FLÜCKIGER and HANBURY, "Hist. of Drugs.")

The quality of opium varies greatly, according to the country where the poppy has grown, the species cultivated, the nature of the season, and the care taken in its collection and preservation. Some varieties are inferior to others, in the ratio of three to one. In the European markets the preference is given to the opium of Smyrna. This sort comes into the market in soft lumps, of greater or less bulk, the surface of which is covered with dock seeds, from the leaves in which they have been folded. It is light coloured internally; but the surfaces, when broken or cut, darken on exposure to the air. The smell is strong and peculiar, and the taste bitter and acrid. It contains 10 to 14 per cent. of morphine.

The opium of Constantinople is found in regular flat cakes or loaves, covered with poppy leaves. It is drier than the Smyrna variety, and even brittle. In the hand it softens, and furnishes a fawn-coloured paste, which turns brown on exposure to the air. It smells like the Smyrna opium, but fainter. Its yield of morphine is 6 or 7 per cent.

The Egyptian or Alexandrian opium comes into the market in small, very dry, and very flat leaves, very clean at the surface, and showing scarcely a trace of the leaves in which they have been folded. Its colour is dark-brown; its fracture clean and shining. It has a very feeble smell, and contains only 3 or 4 per cent. of morphine.

The opium of India is found in rounded masses of a darker hue, and more smooth and soft texture. It has an empyreumatic smell, and a less bitter but more nauseous taste. It is wholly soluble in water, and contains more or less sulphate of lime. Its percentage of morphine is usually 2 to 5, but sometimes reaches 10.

English and German opium resembles the East Indian in appearance, but is lighter in hue, and in quality equals the very best Smyrna. Opium collected in France has yielded 16 to 28 per cent. of morphine. The fickleness of the climate, and above all things the high price of labour, render it very improbable that opium can ever be advantageously cultivated in Western Europe.

Opium is soluble in water, alcohol, and ether, and more readily in proof spirit. It also dissolves in acetic, citric, or any of the vegetable acids in solution. Boiling water dissolves about 41 per cent., holds 50 per cent. in solution, and leaves the remaining 9 untouched.

Indian Opium.—The cultivation of the poppy in British India is confined to the large central Gangetic tract, about 600 miles in length and 1200 miles in depth, which is bounded on the north by Goruckpore, on the south by Hazareebaugh, on the east by Dingepore, and on the west by Agra.

The lands selected for poppy cultivation are generally situated where the facilities for manuring and irrigation are greatest. When the soil is rich the cultivators take a crop of Indian corn, maize, or vegetables off the ground during the rainy season, and then in September dress and manure the ground for the poppy sowings. When the soil is poor, the poppy crop alone is grown; and during the rainy season the ground is dressed and cleaned by successive ploughings, weedings, and manurings.

The produce varies very much with atmospheric

phenomena, as well as with suitability of soil. Thus dews facilitate the flow of juice from the wounded capsule, rendering it abundant in quantity, but causing it at the same time to be dark and liquid. An easterly wind (in this part of the country concomitant with a damp atmosphere) retards the flow of the juice, and renders it dark and liquid.

In the Behar agency the quantity of morphine in the opium ranges from 1·75 to 3·5 per cent., and the amount of narcotine from 0·75 to 3·5 per cent. In the Hazareebaugh district 4·5 per cent. of morphine and 4 per cent. of narcotine have been found, whilst from a specimen of Patna garden opium no less than 10·75 per cent. of morphine and 6 per cent. of narcotine has been obtained. In this last case the poppies were irrigated three times during the season, but no manure was used. The climate in which the Patna garden opium was produced (and which is quite equal in excellence to the finest opium of Turkey or Egypt) was precisely the same as that of the districts furnishing the poorer qualities.

The poppy cultivated in the Benares and Behar agencies is exclusively the white variety (*Papaver somniferum album*). In situations favourable to its growth it attains a height usually of 4 feet. The stem is branched, and is terminated by from 2 to 5 ovate-globose capsules, averaging in size a duck's egg (see Fig. 1). The plant reaches maturity in three and a half months, and the time for its cultivation is exclusively the cold season, extending from November to March. The seed of various districts is changed from time to time.

Fig. 1.





Fig. 2.

The sowing is effected between the 1st and 15th of November, the seed being thrown broadcast over the land. In three or four days the plough is passed over the ground to bury the seed, and the soil again levelled. The whole surface is then divided into square compartments, the sides of which are about 10 feet in length, and are raised and converted into channels for the purpose of irrigation. If heavy showers fall in December, January, and February, two irrigations may suffice, otherwise five or six may be required.

The seed germinates in ten or twelve days, and after the plants have attained a height of 2 or 3 inches, they are carefully weeded and thinned to about 6 inches apart.

In February the plant is generally in full flower, and towards the middle of the month, and just before the time for the fall of the petals, these latter are all carefully stripped off and collected. They are then formed into circular cakes from 10 to 14 inches in diameter and about one-sixteenth of an inch in thickness. The manner in which the leaf cakes are made is as follows:—A circular shallow earthen vessel is slightly heated by being placed inverted over a slow fire. A few petals are then spread upon its heated convex surface, and so soon as the glutinous juice which they contain is seen to exude, others are added to the moist surface, and are pressed down by means of a cloth. As soon as these latter become moist in turn, they receive a similar addition of petals; and in this manner the cake is extended circularly by successive and continuous additions, until it has reached the required dimensions. An iron vessel may be used instead of an earthenware one.

The cakes of petals, known as "leaves," are sorted into three classes according to their size and colour. The smaller and darker-coloured "leaves" are used in forming the inner portions of the shells of opium cakes, whilst the largest and least discoloured ones are kept for furnishing their outside coverings.

In a few days after the removal of the petals the capsules have reached their utmost state of development, and the process of collection commences. This extends from about February 25 to March 25. At about three or four o'clock in the afternoon women and children repair to the fields, and scarify the poppy capsules with sharp iron instruments, termed "nushturs" (see Fig. 2). The nushtur consists of four narrow bars of iron, each of which is about 6 inches in length, and of about the thickness of the blade of a penknife. At one extremity each bar does not exceed a quarter of an inch in breadth; but it gradually expands to about 1 inch broad at the other end, where it is deeply notched. The sides of the notch are somewhat curved and ground to sharp edges, and the external angles are brought to sharp points. The four bars are bound firmly together with cotton, and the points at their cutting extremities are kept one-sixteenth of an inch apart by cotton thread passed between the blades.

In using the nushtur only one set of points is used at a time. The capsule is scarified longitudinally from its base to its summit, the incisions passing generally along the longitudinal eminences outside the capsule (Fig. 1). The scarifications thus made are very superficial, and do no more than traverse the thin pericarp of the capsule. Long experience has shown that this is the most effectual way of operating. Each capsule is scarified from 2 to 6 times, according to its dimensions, an interval of two or three days being allowed between each operation.

The capsules having been thus scarified, the collection of the juice is made at an early hour in the following morning. This is effected by means of instruments called "seetooahs," which are made of sheet iron, and resemble concave trowels. With these the juice is scraped from the surface of the scarifications, until the instruments become filled, when their contents are emptied into an earthen pot which the collector carries by his side.

After the plant has ceased to yield any more juice the capsules are collected, and by pressure an oil is extracted from the seeds, which is used for culinary purposes, and for burning in lamps. Of the dry cake a coarse description of unleavened bread is made, or

it is given to cattle. The capsules deprived of their seeds are used for preparing emollient and anodyne decoctions. The stems and leaves are left standing till dry, when they are crushed into a coarse powder, and under the name of poppy trash employed for packing the opium cakes.

When fresh collected the juice from the capsules presents the appearance of a wet granular mass, of a pinkish colour, and at the bottom of the vessel which contains it is found a dark fluid, resembling coffee infusion, to which the name of "pussewah" is given. The recent juice reddens litmus paper strongly, and acts rapidly upon metallic iron, covering it speedily with an inky crust of ferric meconate. The juice when brought home by the collector is placed in a shallow earthen vessel, which is tilted to such a degree that all the pussewah can drain off, and this position is continued as long as any fluid will separate. The pussewah is set aside in a covered vessel and sent to the Ghazeepore sudder factory.

The opium now requires frequent attendance. It is daily exposed to the air, though never to the sun, and is regularly turned over every few days, in order to insure uniform drying of the whole mass; and this process is persevered in for three weeks or a month; or, in fact, until such time as the drug is within a few degrees of standard consistence.

Standard opium, according to the Benares regulations, is opium which, on being heated at 200° Fahr. until everything volatile is given off, leaves a residue of 70 per cent.

The adulterations practised by the cultivators are very various. The grosser impurities are mud, sand, powdered charcoal, soot, cow-dung, pounded poppy petals, and pounded seeds. All of these substances are readily discoverable by breaking the drug up in cold water, removing the soluble and lighter portions of the diffused mass by decantation, and carefully examining the sediment. Impurities of the above kind are then physically apparent. Flour is a favourite adulterant, but is readily detected: opium thus contaminated speedily becomes sour, it breaks with a peculiar short ragged fracture, the sharp edges of which are dull, and not pink and translucent as they should be; and on squeezing a mass of the drug after immersion in water the starch may be seen oozing from its surface. The application of the iodine test furnishes conclusive proof of the presence of amylaceous compounds. The farina of the potato is not unfrequently made use of, as also are glue and goor (an impure treacle). Their presence may be detected by the odour and consistence they impart to the drug.

In addition to the above, a variety of vegetable juices, extracts, pulps, and colouring matters, are occasionally fraudulently mixed with the opium; such are the juice of the prickly pear (*Cactus dilenii*), the extracts prepared from the tobacco plant (*Nicotiana tabacum*), the *Datura stramonium*, Indian hemp (*Cannabis indica*), &c. The gummy exudations of some plants are used; and of pulps the most frequently employed are those of the tamarind and of the bale fruit (*Ægle marmelos*). To impart colour catechu, turmeric, &c., are used. Morphiometry is the only accurate test, and this is too tedious and expensive to be of practical utility. The colour, aroma, and texture are therefore the commercial criteria of the excellence of the article.

The colour of well-prepared opium is a deep, dull brown when viewed in mass, which becomes a bright chestnut brown when a small portion is spread out in a thin layer on a white surface. It adheres to the fingers, and draws out to a moderate extent, breaking with a ragged fracture; should it, however, contain much pussewah, its ductility is much increased, and it is more glutinous. Its smell is peculiar, and perfectly *sui generis;* it is not unpleasant, and in recently well-prepared opium is somewhat fruity.

In cold water opium breaks down readily into curdy flakes, of the colour of pease soup; these gradually subside, leaving the supernatant liquid of a deep brownish-yellow colour. When broken under water by the hand, the opium adheres moderately to the fingers at first, but is soon entirely diffused. Should it contain gum fraudulently mixed, the latter adheres pertinaciously.

If to a portion of the cold water infusion in a hot tube, a few drops of plumbic acetate solution be added, a dirty grey precipitate of plumbic meconate falls, so copious in quantity as to equal in bulk the fluid in the tube. Ammonia throws down a similar and nearly as abundant precipitate, composed of resin and opium alkaloids; this, on exposure to the air, turns black. Tincture of iodine throws down a brick-red precipitate, and tincture of ferric chloride occasions a similar precipitate, of a somewhat darker colour. These tests may be applied in a few seconds, and the comparative bulk of the precipitates thrown down will enable a judgment to be formed of the amount of opium in a given specimen.

After being duly weighed into store, the opium is kept in large wooden boxes, containing about 10 cwts. each, in which it is, if below the manufacturing standard, occasionally stirred up from the bottom, until it has acquired the necessary consistence. Whilst in these boxes it speedily becomes covered with a thin blackish crust (ulmine), and deepens in colour according to the amount of exposure to air and light which it undergoes. Should the drug be of very low consistence, it is placed in shallow wooden drawers instead of boxes, and is constantly turned over till its consistence reaches 70 per cent.

In making up opium cakes for export, opium is selected which is exactly standard, or very close to it; whilst to compensate for any that may be above the prescribed consistence, some low quality opium is added. The various proportions of each are determined by test assays.

The opium is then transferred to wooden vats, about 20 feet deep, 3½ feet wide, and 1¼ foot deep, situated in the caking room. In these vats it undergoes kneading and admixture by men who wade knee-deep through the opium from one end of the vats to the other, until the contents appear to be of uniform consistence. Two specimens are on the

following morning drawn from each vat; and should the consistence reach the factory standard, caking immediately commences.

Down either side of the room in which the vats are placed are ranged the cakemakers; each man being seated on a wooden stand, and being furnished with a brass cup, forming the half of a hollow sphere, and with a vessel graduated to hold a determinate quantity of fluid.

On the previous evening the leaves requisite for forming the shells of the cakes have been weighed out and tied up in bundles, and have been damped to render them supple.

Down the centre of the room are scales, at which the quantity of opium for each cake is weighed out; and beside the scales are boxes filled with "lewah," for the agglutination of the leaves which form the shells of the cakes.

In forming the "lewah" all opium of inferior quality is used, and all the pussewah received is also employed for this purpose; but in addition to these, a quantity of excellent opium is also expended. These ingredients are broken down in the washings of the men's legs and of the various pots and vessels which have contained opium, and a semi-fluid paste is formed of such a consistence that 100 grains of it, when evaporated to dryness at a temperature of 200° Fahr., shall leave 53 grains of residue.

Matters being thus arranged, the cake-maker receives in his graduated tin the prescribed quantity of lewah for making a single cake; and having by his side a bundle of leaves previously weighed, he rapidly forms in his brass cup the lower segment of the shell of the opium cake, pasting leaf over leaf, until the thickness of half an inch has been obtained, and allowing a certain free portion of the leaves to hang down all round over the sides of the brass cup. The opium is then thrown by a boy into the shell so far prepared to receive it. The cake-maker, holding the opium away from the shell with his left hand, then tucks in round the side leaf after leaf, well smeared with lewah, one over the other, until he has completed the entire circle. The free edges of the leaves are now drawn tightly up, and the opium well compressed within its bag of leaves. The small portion still open at the top is closed by laying on leaf after leaf, and finally a large leaf is wrapped round the whole.

As thus formed a well finished cake resembles a 24-pound shot. It is now rolled in finely pounded poppy trash, and is then placed in an earthen cup and put in the sun to dry. It is exposed for three days, with frequent turning about: if, as is frequently the case, it should become distended and puffy, it is at once torn open, the gas allowed to escape, and the cake again tightly closed. At the end of the third day it is placed (still in the cup) in the cake frames, which are formed of open battens, and allow of a free circulation of air about the cakes.

By the end of July the manufacturing is finished; but the cakes still require much attention. They are constantly turned over, and as mildew collects it is removed by rubbing and rolling them in dry poppy trash.

By October the cakes have become dry to the touch, and have acquired considerable solidity. They are now packed in chests, each of which is furnished with a double tier of wooden partitions, each tier containing twenty compartments for the reception of as many cakes. They are steadied by filling in the interstices with poppy trash.

The above process of manufacture applies to the opium which is put up for the China market, and which includes the great bulk of the entire supply. With the drug intended for internal consumption, and called "abkaree opium," a different process is followed.

The opium intended for abkaree purposes is brought to a consistence of about 90 per cent. by direct exposure to the sun, in which state it is as firm and as easily moulded as wax. It is then formed by means of a mould into square bricks of 1 seer (1 lb. 13 ozs.) weight each. These are wrapped in oiled Nepaul paper, and packed in boxes furnished with compartments for their reception.

The opium put up in this way has not the same powerful aroma as is possessed by that put up in balls.

The manufacture for the season being concluded, six cakes are selected promiscuously by the magistrate of Ghazeepore, for examination and chemical analysis. Of these two are forwarded to the opium examiner at Calcutta, two to the examiner of the Behar agency, and two are reserved for the examiner of the Benares agency.

The examination is directed to the following points:—

1. The gross weight of the cake. 2. The weight of the shell. 3. The weight of the opium. 4. The condition of the shell. 5. The physical character of the drug. 6. Its consistence. 7. The amount of extract taken up from it by distilled water. 8. The quantity of morphine present. 9. The amount of narcotine present.

The average results of the examination of the opium of the Benares agency for four years were:— Residue from 100 grains exposed to a temperature of 200° Fahr., 75·5; extract taken up by distilled water from 100 grains, 47·99; morphine per cent., 3·21; narcotine per cent., 4·06.

A chief chemical feature which distinguishes Bengal opium from that of Turkey and Egypt, is the large proportion which the narcotine in the former bears to the morphine, and this proportion is constant in all seasons.

It is a matter of importance to ascertain whether the treatment which the juice receives after its collection can influence in any way the amount of the alkaloids, or of the other principles contained. In Turkey it is the custom to heat up the juice with saliva; in Malwa it is immersed, as collected, in linseed oil; whilst in Bengal it is brought to the required consistence by mere exposure to air in the shade: though, at the same time, all the watery part of the juice that will separate is drained off,

and used, as has already been explained, in making lewah.

Dr. W. C. B. EATWELL obtained the following results from the analysis of fresh juice, from which none of the pussewah was separated. The analyses have special reference to the amount of morphine and narcotine only.

Analysis of 2000 grains of freshly collected juice, subjected to experiment on the day of collection—

	Grains.
Morphine,	11·1
Narcotine,	32·7
Matters soluble in alcohol,	521·0
Dry marc insoluble in alcohol,	225·2
Water and volatile matter given off at 200° Fahr.,	1210·0
	2000·0

When the juice was dried at 200° Fahr. until brought to the factory standard, the amounts were—

	Grains.
Morphine,	24·9
Narcotine,	30·9
Other matters soluble in alcohol,	546·7
Dry marc,	215·0
Water and matters volatile at 200° Fahr.,	182·5
	1000·0

Lastly, a portion of the juice was placed in a porcelain basin, and left till it acquired solidity. It acquired a consistence of 90·3 per cent., and contained—

	Grains.
Morphine,	26·1
Narcotine,	32·8
Other matters soluble in alcohol,	630·4
Dry marc,	213·7
Water and matters volatile at 200° Fahr.,	97·0
	1000·0

To compare these results it is necessary to suppose the drug to have been reduced to the same state of dryness, when the composition of the three will appear as—

	1.	2.	3.
Morphine,	1·405	3·061	2·890
Narcotine,	4·012	3·795	3·632
Other matters soluble in alcohol,	65·949	66·874	69·811
Dry marc insoluble in alcohol,	28·506	26·301	23·665
	99·872	100·031	99·998

The agreement of results in these three sets of experiments is tolerably close. In No. 1 the amount of morphine is very small, but the quantity of narcotine is larger than in either of the other two cases. The suggestion which this naturally prompts is that the narcotine, during the process of analysis, or during the changes which occur in the juice after its extraction from the plant, is converted into morphine.

The results of the second analysis seem to indicate that the employment of artificial heat, in bringing the drug rapidly to the required consistence, is not detrimental to the narcotic power of the opium.

Pussewah.—Recently collected pussewah is a dark fluid, resembling strong infusion of coffee, and having a peculiar smell. It reddens litmus paper strongly. A solution of plumbic acetate throws down a copious precipitate of plumbic meconate, and lime water has the same effect. Ammonia throws down a plentiful precipitate of a mottled grey colour, which soon becomes uniformly black; and copious dilution with water likewise occasions in it a deep brown precipitate.

Dr. EATWELL found the specific gravity of recently collected pussewah to be 1·120 at 83° Fahr.: 100 grains evaporated to dryness yielded 30 grains of a brownish-yellow residue, emitting an odour something resembling that of Burgundy pitch. After pussewah has become concentrated to about one-third of its original volume, it acquires the consistence of treacle, and as the process of drying goes on still further it becomes quite solid. During the hot and dry months this solid residue acquires resinous hardness, becomes brittle, and breaks with a resinous fracture; but as soon as the weather becomes damp it rapidly absorbs moisture from the atmosphere, becomes jetty black and polished on the surface, and much resembles cobbler's wax.

Pussewah contains some of the most valuable constituents of opium. From 500 grains of solid pussewah, which on evaporation to dryness left 88·9 grains of residue, EATWELL extracted 12 grains of pure narcotine, but only a trace of morphine. In a second analysis of a pussewah, of which 500 grains yielded 85·5 of residue, he obtained 10·6 grains of morphine and 16·9 grains of narcotine.

The Chinese form a watery extract of opium for the purpose of smoking, and recover the whole of the constituents of the pussewah by boiling the shells in water.

Turkey opium is obtained from the *Papaver somniferum*, var. *B. glabrum*. The flowers are purplish or white, the seeds vary from white to dark violet. It is cultivated by peasant proprietors in Asia Minor. The soil must be moist and rich. The seed is sown at intervals between November and March, so that there may be a succession of capsules to operate on.

Flowering takes place between May and July; the incisions are made a few days after the petals have fallen off the flowers. The incisions, as in India, are made in the afternoon, and the exuded juice scraped off next morning by a knife, which the labourer wets with saliva from time to time to prevent the adhesion of the juice to the blade. Each poppy head is cut only once. As scraped off, the poppy juice is laid on poppy leaves and placed in the air to dry in a shady place, and is then wrapped in poppy leaves. There is no settled size for the cakes.

The merchants buy the opium in its natural state; they then separate it into masses of suitable size, wrapping it in poppy leaves, and packing it with cotton or with the fruit of the *Rumex* species, to prevent the lumps sticking together. It is then transported to market in sealed packets. It should contain 12 to 15 per cent. of morphine.

Turkey opium in the English market is found in lumps of from ¼ lb. to 2 lbs. weight; these are

covered with fragments of poppy leaves, *Rumex* chaff, &c. Its consistence is much less than that of Indian opium; it can be cut with a knife, moulded with the fingers. The centre of the lump is moist. Its colour varies from almost black-brown to a light chestnut.

Egyptian opium is of much greater consistence; its fracture is finely porous, of a dark brown colour.

Persian opium is the produce of *Papaver somniferum*, var. γ *album* (*P. officinale*, Gm.) It contains 8 to 11 per cent. of morphine, and is commonly much adulterated.

The poppy plant may be cultivated in most of the countries of Europe. In France, AUBERGIER of Clermont-Ferrand produces an opium which he calls *Affium*, and which contains 10 per cent. of morphine.

Constituents.—The chemical history of opium may be said to have its origin so far back as 1803, when CHARLES DEROSNE, an apothecary of Paris, in diluting a syrupy aqueous extract of opium, observed a crystalline body, in which he believed its narcotic properties to reside. From his description of its properties this substance was obviously narcotine ($C_{23}H_{23}NO_7$). In 1805 SERTÜRNER made the next step in the investigation of opium. He detected meconic acid ($C_7H_4O_7$), and morphia, or morphine, ($C_{17}H_{19}NO_3$). In 1826 DUBLANC discovered meconine ($C_{10}H_{10}O_4$). During the several years following opium was subjected to a very minute investigation by COUERBE, PELLETIER, ROBIQUET, MERCK, and others, who added codeine ($C_{18}H_{21}NO_3$), thebaine ($C_{19}H_{21}NO_3$), narceine ($C_{23}H_{29}NO_9$), and porphyroxine (?) to the list of its crystalline constituents. Subsequent to their time, little was done until 1844, when WÖHLER and BLYTH separately examined narcotine, and made it the starting point of a very remarkable series of products. In 1850 THOMAS ANDERSON (Professor of Chemistry in the University of Glasgow) undertook the study of the principles of opium, and cleared up some of the doubtful points. He found that the varying results obtained by different experimenters greatly depended on the methods they pursued. Some investigators found particular substances abundantly, others in only small quantity; the difference ANDERSON states to be due to modifications in working, which at first sight appear very trifling. Even the quantity of water employed in the primary solution of the opium is important, and greatly affects the quantity of resinoid matters dissolved, and by consequence, the facility with which some of the bases are made to separate in the crystalline condition.

This opinion is borne out by the researches of EATWELL, DECHARME, ADRIAN, and others. DECHARME observed that the amount of morphine diminished when the juice is very slowly dried—a point of great importance, deserving attention in India, the opium from whence is remarkable for its low percentage of morphine. It is extremely probable that the long period during which the juice remains in a wet state (always three to four weeks), goes far to account for the small quantity, through decomposition taking place.

The following table, by FLÜCKIGER and HANBURY, shows the natural alkaloids of opium and a few of their artificial derivatives.

TABLE OF OPIUM ALKALOIDS AND THEIR DERIVATIVES.

Discovered by	
Wöhler, 1844.	*Cotarnine*, ... $C_{12}H_{13}NO_3$ Formed by oxidising narcotine; soluble in water.
Hesse, 1871.	1. HYDROCOTARNINE, ... $C_{12}H_{15}NO_3$ Crystallizable, alkaline, volatile at 100° C.
Matthiessen & Wright, 1871.	*Apomorphine*, ... $C_{17}H_{17}NO_2$ From morphine, by hydrochloric acid. Colourless, amorphous, turning green by exposure to air; emetic.
Wright, 1871.	*Desoxymorphine*, ... $C_{17}H_{19}NO_2$
Sertürner, 1816.	2. MORPHINE, ... $C_{17}H_{19}NO_3$ Crystallizable, alkaline, levogyre.
Pelletier & Thibouméry, 1835.	3. PSEUDOMORPHINE, ... $C_{17}H_{19}NO_4$ Crystallizes with H_2O, does not unite even with acetic acid.
Matthiessen & Burnside, 1871.	*Apocodeine*, ... $C_{18}H_{19}NO_2$ From codeine by chloride of zinc; amorphous, emetic.
Wright, 1871.	*Desoxycodeine*, ... $C_{18}H_{21}NO_2$
Robiquet, 1832.	4. CODEINE, ... $C_{18}H_{21}NO_3$ Crystallizable, alkaline, soluble in water.
Matthiessen & Foster, 1868.	*Nornarcotine*, ... $C_{19}H_{17}NO_7$
Thibouméry, 1835.	5. THEBAINE, ... $C_{19}H_{21}NO_3$ Crystallizable, alkaline.
Hesse, 1870.	*Thebenine*, ... $C_{19}H_{21}NO_3$
Hesse, 1870.	*Thebaicine*, ... $C_{19}H_{21}NO_3$ From thebaine or thebenine by hydrochloric acid.
Hesse, 1871.	6. PROTOPINE, ... $C_{20}H_{19}NO_5$ Crystallizable, alkaline.
Matthiessen & Foster, 1868.	*Methylnornarcotine*, ... $C_{20}H_{19}NO_7$
Hesse, 1811.	*Deuteropine*, ... $C_{20}H_{21}NO_5$
Hesse, 1870.	7. LAUDANINE, ... $C_{20}H_{25}NO_4$ An alkaloid which, as well as its salt, forms large crystals, turns orange by hydrochloric acid.
Hesse, 1870.	8. CODAMINE, ... $C_{20}H_{25}NO_4$ Crystallizable, alkaline, can be sublimed, becomes green by nitric acid.
Merck, 1848.	9. PAPAVERINE, ... $C_{21}H_{21}NO_4$ Crystallizable, also its hydrochlorate, sulphate in sulphuric acid precipitated by water.
Hesse, 1865.	10. RHŒADINE, ... $C_{21}H_{21}NO_6$ Crystallizable, not distinctly alkaline; can be sublimed; occurs only in *Papaver rhœas*.
Hesse, 1865.	*Rhœagenine*, ... $C_{21}H_{21}NO_6$ From rhœadine, crystallizable, alkaline.
Hesse, 1870.	11. MECONIDINE, ... $C_{21}H_{23}NO_4$ Amorphous, alkaline, melts at 58° C.; not stable, the salts also easily altered.
T. & H. Smith, 1864.	12. CRYPTOPINE, ... $C_{21}H_{23}NO_5$ Crystallizable, alkaline; salts tend to gelatinize, hydrochlorate crystallizes in tufts.
Hesse, 1871.	13. LAUDANOSINE, ... $C_{21}H_{27}NO_4$ Crystallizable, alkaline.
Derosne, 1803.	14. NARCOTINE, ... $C_{22}H_{23}NO_7$ Crystallizable, not alkaline; salts not stable.
Hesse, 1870.	15. LANTHOPINE, ... $C_{23}H_{25}NO_4$ Crystals not alkaline, sparingly soluble in hot or cold alcohol, ether, or benzol.
Pelletier, 1835.	16. NARCEINE, ... $C_{23}H_{29}NO_9$ Crystallizable (as a hydrate) readily soluble in boiling water or in alkalies, levogyre.

Morphine, Morphia.—The process originally proposed by ROBERTSON and GREGORY is that which is

most generally adopted:—Macerate 1 lb. of sliced opium with two pints of water for twenty-four hours, decant, and repeat the process with the same quantity of water, subjecting the insoluble residue to a strong pressure. Unite the liquors, evaporate in a water-bath to the bulk of one pint, and strain through calico. Pour in now three-quarters oz. chloride of calcium dissolved in 4 fluid ozs. of distilled water, and evaporate the solution until it is so far concentrated that upon cooling it becomes solid. Envelop the mass in a double fold of strong calico, and subject it to powerful pressure, preserving the dark fluid which exudes. Triturate the squeezed cake with about half-a-pint of distilled water, and the whole being thrown upon a paper filter, wash the residue well with boiling distilled water. The filtered fluids having been evaporated as before, cooled, and solidified, again subject the mass to pressure; and if it be still much coloured repeat this process a third time, the expressed liquids being always preserved. Dissolve the pressed cake in 6 ozs. of boiling distilled water; add quarter oz. of purified animal charcoal and digest for twenty minutes; filter, wash the filter and charcoal with boiling distilled water, and to the solution thus obtained add ammonia solution in slight excess. Let the pure crystalline morphia which separates as the liquid cools, be collected on a proper filter and washed with cold distilled water until the washings cease to give a precipitate with acidulated silver nitrate.

From the dark liquids expressed in the above process an additional product may be obtained by diluting them with distilled water, precipitating with solution of potash added in considerable excess, filtering, and supersaturating the filtrate with hydrochloric acid. This acid liquid digested with a little animal charcoal, and again filtered, gives, upon the addition of ammonia, a small quantity of pure morphine.

The principle involved in this process is very simple. The bases are present in opium chiefly as meconates, which are difficultly crystallizable salts; but on addition of chloride of calcium, calcium meconate precipitates, and the chlorides remain in solution, of which the hydrochlorates of morphine and codeine are readily crystallizable, and separate from the concentrated solution, leaving the bases behind in the mother liquor.

It is from the residue left, after the complete separation of morphine, that the other bases are extracted. ANDERSON proceeds thus:—The mother liquor, which has the consistence of treacle, and is perfectly black, is diluted with water, and ammonia added. An abundant dark precipitate falls consisting of narcotine, papaverine, and thebaine, accompanied by a small quantity of codeine, and all contaminated by a brown resinous substance (*Lanthopine*, HESSE). This precipitate, which is at first quite granular, runs together into a resinous mass, if allowed to lie in the fluid, and the mother liquor is then as effectually squeezed out of it as if it were put into a powerful press.

By solution of this precipitate in boiling spirit, impure crystals of *narcotine* are obtained on cooling, which may be purified by animal charcoal and successive crystallizations. By distilling down the solution a further crop of crystals is dissolved, and finally a dark mother liquor is obtained, from which *thebaine* and *papaverine* may be prepared.

For this purpose water is added; the liquid is rendered slightly acid by acetic acid, and the resin which is thus separated is filtered off. Subacetate of lead is then added to the filtrate until it restores the blue of reddened litmus; and the precipitate being separated, the excess of lead is removed by sulphuretted hydrogen, or, more conveniently, by sulphuric acid. Ammonia then precipitates thebaine, still contaminated with resinous matter, from which it is separated by crystallization from absolute alcohol, and decolorized by animal charcoal.

Papaverine may be extracted from the lead precipitate by digesting it with alcohol, evaporating the liquid, treating it with hydrochloric acid, filtering from resin, concentrating, and leaving the solution to itself for some time, when the sparingly soluble hydrochlorate of papaverine slowly crystallizes. Precipitation with ammonia and crystallization from spirit give the base itself in a state of purity.

The mother liquor, from which the precipitate of these alkaloids has been separated, contains *narceine* and *meconine*, with a small quantity of papaverine. In concentrating it, narceine separates in abundance, and is easily obtained pure by washing with a small quantity of cold water, and by crystallizing two or three times. It is remarkably distinguished by the facility with which it is obtained free from colour. After concentrating the liquid until the narceine is separated, the residue is agitated with ether, which extracts meconine together with a little papaverine.

Meconic acid is prepared from the calcium meconate obtained in the first part of ROBERTSON and GREGORY'S process.

HESSE, who has much extended our knowledge of the rarer opium bases, likewise operates with the mother liquors from ROBERTSON and GREGORY'S process. On addition of excess of ammonia to the mother liquor, diluted with its own bulk of hot water, a resinous precipitate of *lanthopine* is thrown down, the other bases remaining in solution. By the agitation of the filtrate with ether, and of the ethereal extract with acetic acid, a mixture of acetates is obtained. Caustic soda added in excess precipitates *papaverine*, *narcotine*, *thebaine*, some *cryptopine* and *protopine*, *laudanosine* and *hydrocotarnine*, while the alkaline filtrate contains in solution *lanthopine*, *laudanine*, *cryptopine*, and *codamine*. These last are again converted into acetates by the other process, and the liquid is neutralized with ammonia. A little *lanthopine* separates after twenty-four hours, and the filtrate yields with ammonia a precipitate soluble in boiling dilute alcohol. On cooling, crystals of a mixture of *laudanine* and *cryptopine* separate. By evaporation of the alcoholic solution, and treatment with ether, a solution was formed from which codamine was obtained, either by addition of fused

chloride of calcium, which causes water, colouring matters, and crystals of *codamine* to separate, or by conversion into acetate, thence into hydriodide, and purification of the latter.

The precipitate insoluble in caustic soda is digested with dilute alcohol, and acetic acid added till litmus paper is faintly reddened by it. Addition of 3 times the volume of boiling water produces a crystalline precipitate of *papaverine* and *narcotine* (these bases not neutralizing acetic acid). The filtrate freed from alcohol by evaporation, gives, on addition of tartaric acid, a copious crystalline precipitate of *thebaine bitartrate*. The mother liquor of this is neutralized by ammonia, and mixed with 3 per cent. of its weight of sodium bicarbonate made into a paste with water. After about a week a black pitchy mass separates. The filtrate from this gives with ammonia a precipitate which is treated with boiling benzene, the filtrate being also extracted with benzene. *Cryptopine* and *protopine* thus remain undissolved, while on shaking the benzene solution with a saturated aqueous solution of sodium bicarbonate, *laudanosine* crystallizes out, and the benzene filtrate from this, treated with hydrochloric acid gas, yields hydrochloride of *hydrocotarnine*.

The value of opium depends on the moisture present and on the quantity of morphine contained in the dry drug. The water is determined by exposing a known amount to the heat of a water bath until its weight is constant.

For the estimation of morphine many processes have been devised, but none are perfectly satisfactory. HANBURY and FLÜCKIGER recommend that given below.

Take of opium, previously dried at 100° C., 7 to 10 grams., mix it with thrice its weight of coarsely-powdered pumice, and pack the mixture in a percolation tube; then remove by boiling ether the narcotine, together with the wax and colouring matter. The residue should be next moistened (it may remain in the tube) with a very little spirit of wine (0·822), and exhausted with water. The solution is usually a little acid; if otherwise, a little acetic acid should be added to the water. The solution should be about equal to 20 times the bulk of the opium; it is then mixed with ammonia, as small an excess as possible being added. After a repose of a day or two, the morphine will be found in crystals attached to the sides and bottom of the glass. It may be dried and weighed as *crude morphine*, but ought to be re-crystallized from boiling alcohol (0·822) at least once.

There are three principal difficulties in this process—1. It is not easy to remove the whole of the narcotine and wax. 2. It is even less easy to extract the morphine with as little water as is desired; and by using much water, the bulk of the solution is inconveniently increased, and has then to be reduced by evaporation. 3. The purification of the crude morphine is necessary, yet occasions inevitable loss. These sources of error should be kept in view and avoided as much as possible.

OXALIC ACID.—*Oxalsäure, kleesäure*, German; *acide oxalique, acid d'oseille*, French ($C_2H_2O_4$).—From its frequent occurrence in the vegetable kingdom, oxalic acid may have been well known, in one form or another, to the early chemists, or even to some of the alchemists, who very often employed plants in their experiments. No recorded description, however, tallies sufficiently well for identification, until the publication in 1773 of SAVARY'S treatise "De Sale Acetosellæ." In that work is described the action of heat upon the "sal acetosellæ," a salt which had been obtained from the sorrel plants, and is sometimes known in England, even at present, by the name of "salts of sorrel." The products obtained were an acid sublimate and an aqueous distillate, which without doubt consisted, respectively, of anhydrous oxalic acid and an aqueous solution of the same, mixed, perhaps, with formic acid and other substances. The discovery of oxalic acid has frequently been incorrectly ascribed to SCHEELE in ignorance of this work of SAVARY'S. In 1779 WIEGLER made a similar observation to that of SAVARY.

Later on, the celebrated Swedish chemist BERGMAN obtained a crystalline acid as a product of the action of nitric acid upon ordinary sugar. This he believed to be a new substance, and to it he gave the name of "sugar acid;" but shortly afterwards this "sugar acid" was examined by SCHEELE, and shown by him to be identical with the substance obtained previously by SAVARY, and also with a substance he obtained from salts of sorrel by precipitation with subacetate of lead, and subsequent decomposition of the precipitate. From the name of the plant, *Oxalis acetosellæ*, from which the salt was obtained, SCHEELE gave to the substance the name *oxalic* acid, which it has borne ever since. At the same time SCHEELE further studied the properties of the acid, but did not arrive at its composition; and notwithstanding the many attempts of RICHTER, THOMSON, BERZELIUS, and others, it was not till 1816 that DÖBEREINER succeeded in demonstrating its real composition. His results were confirmed and extended by DULONG, BERZELIUS, and others.

In 1829 GAY LUSSAC observed that when wood, starch, and many other organic substances, were heated with caustic alkalies, they disappeared or were changed; and that oxalic acid, as oxalate of the alkali, almost invariably appeared among the products of the action. This observation appears to have remained for a long time an isolated scientific fact, hidden in comparative obscurity, till in 1858 the reaction was reinvestigated quantitatively, and with a view to utilize the method for manufacturing the acid, by POSSOZ, who succeeded in developing a process which has now superseded all others, and one, too, which enables it to be obtained in practically unlimited quantities. Since then, many have investigated the various compounds and reactions, so that oxalic is now one of the best understood of organic acids. It has also become, since the above process, about the least costly of the organic acids, and has accordingly come into extensive use in the various chemical industries.

Occurrence.—The compounds of oxalic acid occur very widely distributed in nature, particularly in the vegetable kingdom; but there seems to be some doubt whether the free acid has yet been found, though some assert that it exists in the juice of the chick-pea, as well as in *Boletus igniarius*.

Several salts of it have occasionally been observed as minerals. Rammelsberg and Mariano de Rivera found a rare mineral from Koloseruk, near Bilin in Bohemia, to consist of hydrated ferrous oxalate. This mineral, called Humboldtite, appears to have occurred in a bed of brown coal or lignite, so that it is doubtful how far it may be indirectly of vegetable origin. The oxalate of *lime* has been described by Greg as the mineral *Conistonite*, of which he gives the following analysis:—

	Per Cent.
Oxalic acid,	28·02
Lime,	21·05
Magnesia and soda,	·82
Water,	49·15

A similar compound was found by Marrat in a Cumberland copper mine; and Sandall has given an account of the occurrence of a deposit of crystals of oxalate of lime upon the surface of crystals of calc-spar, which he called Whewellite. Liebig has also given the name of Thierschite to a grey warty incrustation of the same composition, which is found upon the frieze of the Parthenon at Athens. There is good reason to suspect that these minerals, all of them very rare, may directly or indirectly be of organic origin.

It is particularly in plants that we find oxalates of very general occurrence. It would be tedious and uninteresting to give a complete list of all the species in which the acid has been observed, but it may be useful to mention a few of the commoner plants. The oxalate of potash occurs among others in the wood sorrel (*Oxalis acetosella*), in the common sorrel (*Rumex acetosa*), and in their allied species. It is found also in several species of rhubarb, the acid taste of which, as well as the sourness of the sorrel, is due to the acidity of the binoxalate of potash that they contain. Oxalate of soda has been found in species of *Salsola* and *Salicornia*. But by far the most frequently occurring salt is the oxalate of lime, which in many lichens, especially *Parmelia* and *Variolaria*, forms the bulk of the solid matter. In one species of the former, growing on the sandy desert plains of Persia, which is used by the Kirghis for food, there has been found 66 per cent. of oxalate of lime, together with about 23 per cent. of a mucilaginous body like that contained in Iceland moss. The analysis was, however, made after a drought, otherwise there would have been found more moisture in the plant, which would materially reduce the proportion of the oxalate. But in the great bulk of the plants in which it occurs it is found only in minute quantity; but, on the other hand, though small in amount, it is of almost universal occurrence. It usually forms deposits in the plant-cells, sometimes in isolated, well-developed crystals, or in tufts of needles (*raphides*); sometimes as a conglomerate, grown with the organic matter and attached to the cell-walls (*cystoliths*), or in globular crystalline concretions, or other similar forms. These deposits seem to occur very seldom in *Algæ* or in cryptogamic plants; but in all other phanerogams they occur in abundance, and indeed in almost all other plants without exception. Nor is the separation of oxalate of lime peculiar to any season of the year, or to any particular epoch in the life of the plant, but takes place from the first budding of the plant in spring to the fall of the leaf in autumn. The formations of oxalate of lime in plants have been exhaustively studied by A. von Payen.

In the animal kingdom oxalic acid is not of such general occurrence; but it is found combined with lime in the *Allantois* liquor of the cow, in the mucus of the gall bladder, and in the mucous membrane of the impregnate uterus. Oxalate of lime is also a common constituent of urine, in which it is a frequently occurring sediment; and the "mulberry calculus," which is somewhat common, is almost wholly composed of it. In guano there exists a small quantity of oxalate of ammonia.

Composition and Constitution.—The ordinary crystals of oxalic acid that occur in commerce contain two molecules of water of crystallization, and correspond in composition to the formula $C_2H_2O_4.2H_2O$. They contain:—

	Per cent.
Carbon,	19·05
Hydrogen,	1·59
Oxygen,	50·79
Water,	28·57

The anhydrous acid dried at 100° C. corresponds to the formula $C_2H_2O_4$: when it is attempted further to abstract water from this body, it splits up into carbonic anhydride (CO_2), carbonic oxide (CO), and water, instead of yielding the anhydrous radical C_2O_3, which was formerly assumed or suspected to exist. The fact that this radical (C_2O_3) was intermediate in composition between CO and CO_2, induced Gay Lussac at one time to propose for oxalic acid the name of *hypo-carbonic acid*. As at present regarded, the constitution of the anhydrous oxalic acid may be represented by the formula—

$$C_2O_2\begin{matrix}OH\\OH\end{matrix}$$

containing two hydroxyls, or by—

$$\begin{matrix}CO.OH\\|\\CO.OH\end{matrix}$$

consisting of two carboxyl or oxatyl groups.

Oxalic acid is the first of a series of bibasic acids, having the general formula $C_nH_{2n-2}O_4$, which bear the same relation to the glycols, or diatomic alcohols, that acetic acid does to ordinary alcohol.

From ethylic glycol, oxalic acid may readily be obtained by oxidation. A monobasic acid, glycollic acid, still partly an alcohol, is first produced, but further oxidised to the dibasic oxalic acid thus:—

Glycol.		Glycollic acid.		Oxalic acid.
$\left\{\begin{matrix}CH_2.HO\\CH_2HO\end{matrix}\right.$	....	$\left\{\begin{matrix}CO.HO\\CH_2HO\end{matrix}\right.$	....	$\left\{\begin{matrix}CO.HO\\CO.HO\end{matrix}\right.$

Oxalic acid is also intimately related to cyanogen; for when an aqueous solution of that gas is kept for some time, ammonium oxalate is formed by assimilation of water according to this equation—

$$2CN + 4H_2O = (NH_4)_2C_2O_4$$

By heating sodium formate, hydrogen is evolved and sodium oxalate remains, thus:—

$$2\begin{Bmatrix} H \\ CONaO \end{Bmatrix} = H_2 + \begin{Bmatrix} CONaO \\ CONaO \end{Bmatrix}$$

By the decomposition of albuminous bodies oxalic acid is formed along with numerous other substances. The oxalic acid in animal fluids is doubtless due to some action of this kind. Uric acid is probably the intermediary stage of the oxidation of albumen immediately prior to the formation of oxalic acid; for when uric acid is oxidised, oxalic acid and allantoin are produced.

When metallic sodium, mixed with quartz sand to increase the surface exposed, is heated to the temperature of boiling mercury in presence of an excess of dry carbonic anhydride, the latter is absorbed, and a mottled grey mass results, consisting mostly of sodium oxalate, with a little unchanged sodium (DRECHSEL). The reaction may be represented thus:—

$$\begin{matrix} CO.O \\ CO.O \end{matrix} + 2Na = \begin{Bmatrix} CO.ONa \\ CO.ONa. \end{Bmatrix}$$

This reaction takes place to some extent in the manufacture of potassium. The oxalic acid in plant cells is probably reduced from carbonic acid and water in an analogous manner, oxygen being evolved by the reducing action of the solar rays, thus:—

$$2CO_2 + H_2O = \begin{Bmatrix} CO.OH \\ CO.CH \end{Bmatrix} + O.$$

Besides this reaction, in which oxalic acid is formed by reduction from carbonic anhydride, there are very many others in which, on the other hand, the acid is produced as the last stage of oxidation of carbonaceous substances, prior to their final oxidation into carbonic anhydride, which is the highest oxidised carbon compound. This oxidation may be effected by several agents. By treatment with nitric acid very many substances yield oxalic acid; while others again, by melting with caustic alkali, evolve hydrogen and combustible gases, and a kind of oxidation is thus effected, oxalic acid being formed and remaining combined with the alkali. In these cases the action is destructive, the products having no simple chemical relation to the substance treated.

By oxidation oxalic acid gives carbonic acid and water, thus:—

$$C_2H_2O_4 + O = 2CO_2 + H_2O.$$

This reaction actually occurs with an aqueous solution exposed to the air in presence of platinum black (DÖBEREINER), and it is said that a very dilute solution of oxalic acid is spontaneously oxidised (BIZIO). According to CARLES the aqueous solution is dissociated at 100° C., carbonic acid and formic acid being carried off when a stream of nitrogen, oxygen, or hydrogen is passed through the hot fluid.

It will thus be seen that oxalic acid is at once the first stage of the building up of complex organic bodies, by reduction from carbonic acid; and inversely, the last stage of the oxidation of many carbonaceous compounds prior to their ultimate conversion into carbonic acid and water.

PREPARATION.—In the laboratory oxalic acid is most conveniently prepared by treating pure white sugar with eight times its weight of nitric acid (1·38 specific gravity) in a large flask, and as the action becomes sluggish, gently warming in a good draught, till no more fumes are evolved. The mixture is then evaporated to one-sixth of its original volume, and allowed to cool and crystallize. The mother liquor on evaporation yields a further crop of crystals. After draining and washing with a small amount of water, the product is recrystallized till free from nitric acid. To obtain the maximum yield the above proportions are necessary, for less nitric acid or weaker acid will not completely oxidise the sugar, and there remains on evaporation a thick liquid from which the oxalic acid crystallizes slowly and with difficulty; while with stronger acid, especially by rapid heating, a part of the oxalic will be further oxidised to carbonic acid and lost. If a weaker acid be employed than that above specified a proportionately larger quantity must be taken. Great care must be taken in heating sugar with a stronger nitric acid, or the action will become very violent and unmanageable.

To obtain the pure anhydrous acid for analytic purposes, it may readily be prepared by sublimation in a current of air after the following manner:—A copper tube 2 inches wide and 20 inches long is soldered in a horizontal position in a copper bath, the ends projecting about an inch beyond the bath. One end is connected with the wide neck of a large tubulated retort by means of an india-rubber ring. Into the tubulus of the retort is inserted a short wide glass tube tightly packed with cotton wool, and this tube is connected with a SPRENGEL water-pump or other constant aspirating apparatus. The copper bath surrounding the tube is filled with paraffin, and the temperature maintained as accurately as possible at 157° C. If allowed to rise to 160° C. vigorous decomposition of the acid ensues, and moisture, resulting from the decomposition, appears in the retort. Into the open end of the copper tube anhydrous oxalic acid, which has been dried by exposure to a temperature of 60° to 70° C., is introduced with a spoon, and the tube closed with a loosely fitting cork, the SPRENGEL pump or aspirator working in the meanwhile. From time to time more dry acid is put into the tube. The vapours of oxalic acid are carried away to the place of condensation by the current of air almost as soon as they are formed, and in the neck of the retort there form beautiful lustrous crystals an inch or more long, while on the curved sides of the body of the retort a white snow-like deposit takes place. Traces of acid are carried along in the stream of air, and if

not for the tube of cotton wool, would speedily obstruct the suction tube of the aspirator. In this way the sublimation proceeds with extraordinary ease, it being only necessary to regulate exactly the temperature of the paraffin bath; while by introducing fresh acid into the tube the operation may be continued as long as may be desired.

Small quantities of the sublimed acid may be obtained in the laboratory by heating the previously dried acid in a beaker glass, or other suitable vessel; but without the current of air it is scarcely possible to obtain any quantity without heating to such a temperature that part of the oxalic acid will be decomposed, and the product contaminated with water and formic acid.

Properties.—The hydrated oxalic acid is a colourless odourless body, crystallizing with two molecules of water of crystallization in beautiful large transparent monoclinic prisms. Exposed to dry air, or *in vacuo* over sulphuric acid, the crystals lose water, become opaque, and finally become a white powder. Exposed to the air at a temperature of 60° to 70° C. in a thin layer, they lose their water, become opaque, and easily fall to pieces between the fingers; and after some hours become anhydrous. If heated at once to 98° C. the hydrated acid fuses in its water of crystallization, and is then much more difficult to dry completely than if heated to a lower temperature. The specific gravity of the crystals is 1·641 at 3°·9 (Joule and Playfair), their cubical expansion from 0° to 100° C. is ·02748. They dissolve readily in water, one part requiring 10·46 parts of water at 14°·5 C. (Nichols). Under the barometric pressure of 718 m.m. 100 parts of water dissolve the following amounts at the temperatures given (Alluard).

8	parts at	10° C.
13·9	"	20°
23	"	30°
35	"	40°
51·2	"	50°
75	"	60°
117·7	"	70°
204·7	"	80°
345	"	90°

The specific gravity of the aqueous solution of different strengths for the temperature 17°·5 C. is given in the following table (Franz):—

Percentage Crystallized Acid.	Specific Gravity.	Percentage Crystallized Acid.	Specific Gravity.
1	1·0032	7	1·0204
2	1·0064	8	1·0226
3	1·0096	9	1·0248
4	1·0128	10	1·0271
5	1·0160	11	1·0289
6	1·0182	12	1·0309

The solution has an intensely sour taste, even when very dilute; the acid dissolves in 2½ parts of cold, and more readily in boiling alcohol.

According to Kerkhoff, if an aqueous solution of oxalic acid saturated at 100° C. be kept at a steam heat of 100°, but without boiling, it gradually loses acid by volatilization. The acid, which has previously been rendered anhydrous by exposure to a temperature of 60°, begins to sublime at about 100° C., so that if heated in a water bath, a white deposit will be found on the cooler parts, and where the current of heated air has impinged. Volatilization takes place much more rapidly at 150° to 155° C., especially in a current of air; but decomposition commences pretty vigorously at 160° C. The pure anhydrous acid may readily be prepared by sublimation, as described above. The dry acid absorbs water greedily from the air, its crystals rapidly losing their lustre, but retaining their shape, and becoming converted into the hydrated acid. Dissolved in water, it also gives the hydrated acid. When quickly heated to 180° C. it fuses, and at 190° begins to boil and decompose. The residue not volatilized is unchanged acid. When pure, oxalic acid is in the cold entirely odourless; but its vapours have a powerful irritant action on the mucous membrane of the nose and air passages, exciting violent sneezing and coughing. In comparatively large doses, of a quarter or half an ounce or more, it acts as a powerful poison when taken internally. A dose of half an ounce was taken in solution by a gentleman. There was immediate pain in the throat and stomach, not relieved by drinking water. Vomiting followed, attended soon after with excruciating pain and violent spasms; the tongue was swollen and breathing difficult; the pulse almost imperceptible; the limbs cold and livid. The vomit was tinged with blood. At this stage death usually occurs; but in this case the symptoms abated, and death followed fourteen days after from starvation, the result of the local action of the poison on the throat and stomach. When much diluted a large dose causes death by paralyzing the heart; while a lesser dose diluted often produces tetanus. It appears from experiments that, even in small doses, it does injury when repeatedly administered.

Oxalic acid is one of the strongest acids; its solution in 2000 parts of water still exhibiting a marked acid reaction. It is capable of displacing most acids from their combinations; and even the strongest mineral acids are, under certain circumstances, liberated from their salts by it. In its reactions it shows itself as a very stable and simple reducing agent. It is not readily oxidised by even strong nitric acid, from which, indeed, the anhydrous acid may be obtained crystallized in rhombic octahedra, by saturating the gently warmed acid, and cooling, although prolonged boiling effects complete decomposition. Dilute solutions of oxalic acid, and solutions of oxalates, readily develop organic growths when exposed to air and light.

If 6 parts of pure prussian blue are triturated with 1 or 2 parts oxalic acid and a small quantity of water, and 64 parts of water added, there is formed a dark blue syrupy fluid, which, with a larger quantity of water, gives a clear dark blue solution. The blue ink invented by Stephen and Nash is composed of such a solution. The solubility of prussian blue is much greater when it is perfectly pure and free from the alkali which it usually con-

tains. Six parts of prussian blue, which have been purified by treatment with concentrated hydrochloric acid, with 1 part oxalic acid and 250 of water, give a solution which completely passes through the filter; and if the prussian blue has previously been turned white with strong sulphuric acid, and afterwards washed, 1 part of oxalic acid will suffice to render 8 parts of it soluble. If the solution is to be used as ink there must be added a certain amount of the solution obtained by boiling shellac and carbonate of potash in equal parts with water.

Reactions.—When crystallized oxalic acid is gently heated it loses its water, as described above, and becomes anhydrous. When, however, the heating is rapid, another and quite different result is obtained. As soon as the temperature rises to 150° C. decomposition commences rapidly, carbonic acid and carbonic oxide gases are given off, and some formic acid produced, the following reactions appearing to take place simultaneously—

$$C_2H_2O_4 = CO_2 + CO + H_2O$$
$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

The proportion of CO to CO_2 is about 5 : 6 by volume, showing that the first decomposition happens to five times the extent the latter does. However quickly the heating be conducted, no carbon is separated under any circumstances, the acid volatilizing without residue, in this being distinguished from other non-volatile organic acids. Even when the acid is passed through a redhot tube it is still wholly resolved into gaseous bodies, CO, CO_2, and H_2O, no carbonaceous or other deposit taking place.

The dehydrated acid begins to decompose before fusion, when heated to 165° C. the greater part, however, sublimes unchanged; it boils at 190° C., and can be fused at 180°. The gas evolved is a mixture of CO_2 and CO, the former in greater excess the higher the temperature of decomposition, water and formic acid being simultaneously produced.

When heated with an equal weight of glycerine the hydrated acid evolves only carbonic acid gas if the temperature be kept between 70° to 90° C.; the liquid product in the retort yields, on distillation, first a weak aqueous formic acid, but afterwards strong formic acid. The residue then left in the retort is chiefly unaltered glycerine, to which fresh oxalic acid may be added and the process repeated indefinitely. This is the method employed for producing formic acid for commercial purposes. Other polyatomic alcohols than glycerine will effect the same decomposition, as, for example, ethylene glycol, octylene glycol, erythrite, mannite, dulcite, and quercite (Lorin). Lorin supposes that an oxalic ether of the alcohol is first formed, which on decomposition in presence of water regenerates the alcohol with evolution of formic acid.

Dehydrating agents, or substances which abstract the elements of water, act upon oxalic acid in a similar manner to heat. With concentrated sulphuric acid it is unaltered in the cold, and anhydrous acid may even be obtained crystallized from solution in the gently warmed liquid. But when oxalic acid, or any oxalate, is heated to over 110° with oil of vitriol, decomposition quickly ensues, thus:— $H_2C_2O_4 = H_2O + CO_2 + CO$, a mixture of CO_2 and CO in equal volumes being evolved, the water remaining with the sulphuric acid. This reaction affords a ready means of obtaining carbonic oxide, the carbonic acid being absorbed by milk of lime or caustic alkali. Phosphoric acid produces the same decomposition when heated, and pentachloride and trichloride of phosphorus give the same at however low a temperature the experiment be made. Hence it is very likely that the compound C_2O_3 cannot exist under any accessible conditions.

With chlorine the dry acid combines to form the compound $C_2H_2O_4,Cl_2$. This body is decomposed by water into hydrochloric and carbonic acids. The same products are formed directly by the action of chlorine on the hydrated acid, or upon its solution. Bromine only acts on solutions of oxalates when heated to 50° or 60° C.

With aqueous iodic acid, when heated, iodine is liberated thus:—

$$5C_2H_2O_4 + 2HIO_3 = 10CO_2 + 6H_2O + I_2.$$

Light has great influence on this reaction, and hydrocyanic acid prevents it. Periodic acid is decomposed only slowly, even at a boiling heat. Hydrochloric acid is without action under any circumstances.

When a mixture of powdered oxalic acid with common salt, or chloride of calcium, is heated, hydrochloric acid is evolved and sodium oxalate formed, the salt being completely decomposed. The same reaction takes place in solution, a mixture of boiling saturated solutions of oxalic acid and of salt, in equivalent proportions, depositing crystals of sodium oxalate. Sodium nitrate is also decomposed by oxalic acid, acid sodium oxalate crystallizing out. A solution of sulphate of lime is rendered turbid in a few minutes by addition of oxalic acid. The ability of oxalic acid thus to decompose sulphate of lime, is the reason why it is necessary to employ so large an excess of sulphuric acid to decompose oxalate of lime in the manufacturing process.

Oxalic acid in solution readily decomposes fluor spar, evolving hydrofluoric acid. It decomposes the phosphates of iron, silver, zinc, and copper, and the arseniates of iron, silver, and copper. It also dissolves the sulphides of iron and manganese, but not the sulphides of zinc, cadmium, uranium, cobalt, mercury, or copper. Most chromates are decomposed by it, the liberated chromic acid being reduced at the same time, especially if the liquid be heated. Chromate of zinc first dissolves with yellow colour, but after a time, more quickly when heated, oxalate of zinc separates, and oxalate of chromium remains in solution. The chromates of barium, bismuth, mercury, and lead, are immediately decomposed without previous solution; but chromate of lead, after being strongly heated, is but little attacked. Terchloride of antimony is decomposed, the precipitate being free from chlorine, and only slowly decomposed by boiling water. Finely pounded glass

is rapidly attacked by oxalic acid, the lime and alkali being dissolved and the silica separated. Many minerals are also attacked by oxalic acid, and its presence in lichens probably contributes to the decomposition of rocks (J. W. Slater).

By most oxidising agents oxalic acid is converted into carbonic acid and water, as, for example, by nitric acid, chlorine, hypochlorous acid, permanganate of potassium, chromic acid, and the salts of easily reducible metals, such as the chlorides of gold and platinum, which metals are readily precipitated from their solutions by oxalic acid in sunlight. With metallic oxides and hydrates oxalic acid forms oxalates, except when the oxide is unstable or easily reduced, as is the case with oxide of gold, where the metal is separated and the oxalic acid oxidised. Metallic peroxides are reduced to salifiable oxides, and an oxalate of the resulting oxide is formed by the excess of oxalic acid, as with dioxide of lead and black oxide of manganese. A mixture of 4 parts dry oxalic acid and 21 of dioxide of lead becomes redhot on trituration; carbonic acid, water, and carbonate of lead being the only products. When treated in the usual manner in presence of excess of mineral acid, with permanganate of potash, chromic acid, or metallic peroxides, the oxalic acid is wholly converted into carbonic acid and water at the expense of the oxidised compound used, while a salt of the reduced oxide is formed by the acid present, as in the following example with peroxide of manganese—

$$MnO_2 + H_2SO_4 + H_2C_2O_4 = 2CO_2 + 2H_2O + MnSO_4.$$

When oxalates are heated with caustic potash or hydrate of barium, hydrogen is evolved and alkaline carbonate formed, thus:—

$$2Na_2C_2O_4 + 4KHO = 2Na_2CO_3 + 2K_2CO_3 + 2H_2.$$

But *anhydrous neutral* oxalates, heated by themselves or with *dry* baryta, evolve carbonic oxide, and give a mixture of metallic oxide and barium carbonate, thus:—

$$Na_2C_2O_4 + BaO = BaCO_3 + Na_2O + CO.$$

Potassium and sodium, gently heated with the dry acid, decompose it with vivid combustion, yielding charcoal, alkali, and hydrogen. Potassium decomposes many anhydrous oxalates with loud explosion.

When oxalic acid is acted upon by hydrogen, evolved by sodium amalgam in aqueous solution, or from the action of zinc on dilute sulphuric acid, glyoxylic acid is produced, thus:—

$$\underset{\text{Oxalic Acid.}}{C_2H_2O_4} + 2H = \underset{\text{Glyoxylic Acid.}}{C_2H_4O_4}.$$

Oxalate of ammonia in solution quickly reduces bichloride of mercury to calomel when exposed to light, carbonic acid being simultaneously evolved, thus:—

$$(NH_4)_2C_2O_4 + 2HgCl_2 = 2HgCl + 2NH_4Cl + 2CO_2.$$

Principal Compounds.—There are several series of salts of oxalic acid—1st, normal or neutral salts, of the general formula, $M_2C_2O_4$*; 2nd, acid or hydrogen salts (binoxalates), MHC_2O_4; and 3rd, hyperacid salts, $MHC_2O_4.H_2C_2O_4$. (quadroxalates). Besides salts of these types, containing only one metal, oxalic acid forms many double and even triple salts. Oxalates mostly contain water of crystallization, which is retained with considerable obstinacy. Some of the alkaline salts are very soluble in water, but most others are either insoluble or almost so.

Potassium Oxalates.—The neutral salt is obtained by saturating oxalic acid with carbonate of potash, and evaporating to crystallization. The crystals are white, dissolve in three times their weight of water, and contain 1 molecule of water of crystallization, $K_2C_2O_4.H_2O$, which is only expelled at a temperature of 160° C. It is neutral to test paper.

The acid salt or binoxalate, $KHC_2O_4.H_2O$, is obtained by dividing a solution of oxalic acid into two equal parts, saturating one part with carbonate of potash, and adding the other. If the acid be concentrated, the salt will be precipitated in fine grains. The salt obtained on evaporation may be made anhydrous by rapidly cooling the solution; but when slowly cooled, the product contains 1 atom of water of crystallization. This salt is identical with *sal acetosellæ*, the salts of sorrel of the shops, and is employed for removing ink stains and iron mould from linen, being often sold for that purpose under the misleading name, "salt of lemons." It is comparatively insoluble in cold water. One hundred parts of water dissolve the following amounts of the anhydrous salt at the temperatures given (Alluard):—

C.	Parts.	C.	Parts.	C.	Parts.
1°	2·2	40°	10·5	80°	34·7
10°	3·1	50°	14·8	90°	42·9
20°	5·2	60°	20 5	100°	51·5
30°	7·5	70°	27·1		

The quadroxalate, or "superoxalate," of potash is obtained by saturating one-fourth of a solution of oxalic acid with carbonate of potash, and adding the remaining three-fourths; or by adding a hot concentrated solution of 75 parts of potassium chloride to a hot solution of 252 parts of the crystallized oxalic acid. In the latter case a copious deposit of the quadroxalate is formed on cooling in hydrated crystals, containing $KH.C_2O_4.H_2C_2O_4.2H_2O$. The adhering potassium chloride and acid may be washed away with cold water, in which the salt is but sparingly soluble, requiring 55 parts of water at 8° for solution. The crystals retain their water of crystallization till heated to over 128° C. This salt has sometimes been sent into the market by mistake for salts of sorrel.

Ammonium Oxalates.—There are three ammonium salts analogous to those of potassium, and prepared in the same manner. The neutral salt, $(NH_4)_2C_2O_4.H_2O$, forms rhombic crystals, soluble in 3 parts of cold water; but much less soluble in presence of ammoniacal salts, so that chloride of ammonium precipitates it from concentrated solutions. Heated on the water bath it loses its water, becomes anhydrous, and if further gently heated, is

* In which M represents an atom of a monad metal or positive radical.

decomposed; water, carbonic acid, carbonic oxide, and ammonia distilling off, while the residue contains, besides undecomposed oxalate, a quantity of oxamide, and at a certain stage of the decomposition, oxamic acid. Hydrocyanic acid is also given off. The following equations explain the formation of these bodies:—

Ammonium Oxalate. Oxamide. Water.

$$\begin{matrix}\{CO.ONH_4\\ \{CO.ONH_4\end{matrix} = \begin{matrix}\{CONH_2\\ \{CONH_2\end{matrix} + 2H_2O.$$

$$\begin{matrix}\{CO.ONH_4\\ \{CO.ONH_4\end{matrix} = CO_2 + CO + 2NH_3 + H_2O.$$

$$(NH_4)_2C_2O_4 = CO_2 + HCN + NH_3 + 2H_2O.$$

Towards the end of the heating, carbonate of ammonia sublimes together with a quantity of oxamide. A trace of carbon is left behind. When dissolved in hot water, oxalate of ammonia gives off a little ammonia, so that the solution, which is normally quite neutral, reddens litmus paper.

The acid salt, $NH_4H.C_2O_4.H_2O$, falls as a crystalline precipitate, when oxalic or a strong mineral acid is added to solution of the neutral salt. It is also deposited when warm solutions of oxalic acid and chloride of ammonium are mixed. It is soluble in 16 parts of water at 11° C.; and when heated undergoes aqueous fusion, loses water, and becomes solid. Further heated it becomes pasty, and between 220° and 230° C. swells up and decomposes, evolving CO_2 and CO, and yields an aqueous distillate, containing formic acid and a small sublimate of oxamide. After the evolution of gas has ceased a yellow substance comes off, together with carbonate and cyanide of ammonium. The residue then is a pale yellow mass of oxamic acid, containing small quantities of oxamide and unaltered acid oxalate. The oxamic acid is formed by abstraction of water from the acid oxalate of ammonia thus:—

Acid Oxalate Ammonia. Oxamic Acid.

$$NH_4.H.C_2O_4 = \begin{matrix}\{CO.NH_2\\ \{CO.HO\end{matrix} + H_2O.$$

The quadroxalate is isomorphous with the potash salt, and like it contains 2 molecules of water, which it loses at 100° C. It dissolves in 39 parts of water at 7° C.

Sodium Oxalates are produced similarly to the potash salts. There is no quadroxalate of sodium. The neutral salt is much less soluble than the corresponding potash salt, and crystallizes in the anhydrous state as $Na_2C_2O_4$. It dissolves in 31 parts of water at 15° C., and in 16 parts of boiling water. It does not form good crystals.

The acid salt is obtained in small hard crystals of the composition $NaH.C_2O_4.H_2O$, which are permanent in the air and in vacuo over sulphuric acid; but lose their water on the water bath, and at 160° lose oxalic acid. It is soluble in 60 parts of cold and in 47 parts of boiling water. The solution does not crystallize well.

There are no double salts of oxalic acid, containing potash and soda or ammonia mixed.

Calcium Oxalates.—The neutral oxalate, CaC_2O_4 + Aq, contains water of crystallization, sometimes 1 molecule, sometimes 3 molecules; but dried at 100° it invariably retains only 1, which is not completely expelled except at a temperature considerably over 200° C. The dried salt, which is remarkably electrical, quickly reabsorbs this 1 molecule of water from the air. When oxalic acid or any oxalate in solution is added to a neutral, or not very strongly acid solution of a salt of lime, the precipitate which forms is oxalate of lime; from strong and hot solutions, the monohydrated; but from cold very dilute solutions, the trihydrated salt. The white precipitate is insoluble in water or alkaline solutions, or in acetic acid, chloride, or nitrate of ammonium, either hot or cold; or in even hot concentrated solutions of the chlorides of potassium, sodium, barium, strontium, and calcium. Is insoluble in solutions of oxalates. It is the most insoluble compound of calcium (Liebig). Requires 500,000 parts of water for solution (Malaguti, "Ann. Ch. et Phys." iii. 51, 347). It is nearly insoluble in free oxalic acid, and only dissolved with difficulty by dilute mineral acids, but easily when the acid is strong and in considerable excess. From its great insolubility this compound is of great importance in analytic chemistry, as calcium is usually precipitated for quantation as oxalate. It is hence important to know that it is soluble in solutions of magnesium and manganese, from which, however, it is precipitated by excess of alkaline oxalate; and that it is decomposed by boiling with solutions of copper, silver, lead, cadmium, zinc, nickel, cobalt, strontium, or barium (Reynoso). Oxalate of lime cannot be precipitated for quantitative purposes from solutions containing chromium. aluminium, or ferric iron, as somewhat soluble double salts are formed. A neutral aqueous solution of oxalate of alumina is even not precipitated at all by chloride, nitrate, or hyposulphite of calcium. Normal citrate of soda also dissolves oxalate of lime.

The precipitate obtained from neutral solutions of chloride of calcium and potassium oxalate consists, after drying in the air, of monohydrated oxalate of lime. The crystals occurring in plants (*vide* Occurrence, *ante*) consist of $CaC_2O_4.3H_2O$.

The solution of oxalate of lime in warm nitric and dilute hydrochloric acids deposits crystals of oxalate of lime, monohydrated or trihydrated, according to the degree of concentration.

The saturated solution in warm concentrated hydrochloric acid gives on cooling double oxalochlorides of lime, consisting of $4CaC_2O_4.CaCl_2.24H_2O$ (Souchay and Lenssen); but of $CaC_2O_4.CaCl_4.7H_2O$, according to Fritzsche. The latter salt was probably obtained under different conditions to the former. There is no acid oxalate of calcium known.

Strontium Oxalate is obtained as a precipitate on addition of oxalic acid, or an oxalate, to strontium solution. It is composed of $2(SrC_2O_4)5H_2O$, and loses water of hydration below 100°, but is not rendered anhydrous by a lower temperature than 150° C. It is soluble in 12,000 parts of water, more

soluble in ammonia. The acid salt, $SrH_2(C_2O_4)_2.2H_2O$, has been obtained.

Barium Oxalate resembles oxalate of lime, has the composition $BaC_2O_4.H_2O$, and dissolves in 2590 parts cold water, more readily in sal ammoniac and acetic acid. Precipitated from hot solutions, it has only half the above amount of water; it becomes anhydrous only at 150°. The acid salt is obtained by dissolving the neutral oxalate of barium in hot strong oxalic acid, or by adding together hot solution of barium chloride 122 parts, and oxalic acid 126 parts. It is composed of $BaH_2(C_2O_4)_2.2H_2O$. It dissolves in 392 parts of water at 17° C. Boiling water abstracts acid, leaving the neutral oxalate.

Magnesium Oxalates.—When oxalate of potash and magnesium sulphate are mixed, this compound forms but slowly, though more rapidly on agitation of the liquid, as a crystalline precipitate. It is best prepared, however, by adding *magnesia alba* to saturation to oxalic acid—that precipitated by oxalate of potash always retains potash. It has the composition $MgC_2O_4.2H_2O$, and is soluble in 1500 parts of cold or 1300 of boiling water. It loses 1·5 per cent. of water at 100°, but does not become anhydrous till 150°, at which temperature it is partially decomposed. There is no acid oxalate known, nor any double salt with sodium; but a potassio-magnesic oxalate, $MgC_2O_4.K_2C_2O_4.6H_2O$, is obtained by boiling precipitated magnesic oxalate with a strong solution of oxalate of potash, and cooling the filtrate. There are also known the following double ammonium salts:—

1. $MgC_2O_4.6(NH_4)_2C_2O_4.9H_2O$.
2. $5MgC_2O_45(NH_4)_2C_2O_4.24H_2O$.
3. $MgC_2O_4.5(NH_4)_2C_2O_4.8H_2O$.
4. $MgC_2O_4.7(NH_4)_2C_2O_4.8H_2O$.
5. $3MgC_2O_4.(NH_4)_2C_2O_4.2H_2O$.

and probably others.

Manganese Oxalates.—Hot solutions of oxalic acid added, till a precipitate begins to form, to a hot solution of manganese deposit on cooling white octahedral crystals of the composition $MnC_2O_4 + 2H_2O$; but cold solutions give rose-coloured prismatic crystals containing 3 atoms of water of crystallization. The latter salt loses 1 atom of water when dried in the air, turning white; but when dried *in vacuo* or by heat it remains red, although still losing water. The precipitate obtained by oxalate of potash in a 2 or 3 per cent. solution of manganese sulphate is in pale violet scales containing, like the rose-coloured salt, $MnC_2O_4.3H_2O$; this is unaltered in the air, but in the water bath turns white, and is converted into the 2 atom salt (CROFT,* GEORGEU †). The latter requires about 2500 parts of cold water for solution, and half that of hot water; but dissolves more readily in presence of small quantities of oxalate of potash or ammonia.

A series of complex double ammonium salts, analogous to those of magnesium, have been described by SOUCHAY and LENSSEN.

Potassio-manganous oxalate, $K_2C_2O_4.MnC_2O_4.2H_2O$, is obtained in reddish crusts by cooling a solution of manganous oxalate in hot oxalate of potash.

Potassio-manganic oxalate is obtained thus—Saturate 3 parts of oxalic acid with carbonate of potash, add 4 parts oxalic acid, and then black oxide of manganese until the liquid has only a faint acid reaction. The purple liquid thus obtained is decomposed by heat and by light, and when mixed in the dark with alcohol deposits purple red crystals which cannot be dried without decomposing.

There appears to be no sodio-manganous oxalate.

Zinc Oxalate ($ZnC_2O_4.2H_2O$) is produced as a white powder by the action of oxalic acid upon zinc, or by precipitating a solution of zinc with oxalic acid or an oxalate. It is insoluble in water, in solutions of oxalates, and in neutral solutions, except in presence of ammonium salts. It forms double salts with ammonia and potash.

Cadmium Oxalate (CdC_2O_4) is anhydrous, but otherwise similar to that of zinc. It forms in addition a number of complex ammonio-oxalates, like magnesium and manganese, which are not given by zinc.

Chromium Oxalates.—Chromium forms many variously modified oxalates. An insoluble variety is precipitated as a green pulverulent precipitate, on adding chromium chloride and oxalate of ammonia together. Another kind is obtained by saturating oxalic acid in the cold with precipitated chromic oxide, when a cherry solution is obtained, which on spontaneous evaporation gives an amorphous gum-like mass of a dark colour, transmitting red light at the edges. By boiling the red solution it changes to a green variety, which on evaporation yields a green deliquescent mass. These solutions are not precipitated either by ammonia or calcium salts; but with hot potash they are decomposed, as well as by lime water. When to these solutions alkaline oxalates or earthy oxalates are added, two series of double oxalates are produced from each of them. Those from the green solution are blue, and have the general formulæ,* $Cr.M'_3(C_2O_4)_3$, and $Cr_2M''_3(C_2O_4)_6$. The red solution gives red salts, of the types $CrM'.(C_2O_4)_2$, and $Cr_2M''(C_2O_4)_4$. For example, when a boiling solution of acid oxalate of potash is saturated with chromic oxide (or dissolving 1 part bichromate of potash and 2 of acid oxalate in 1 part water, and adding 2 parts of oxalic acid), there results a solution which gives fine black monoclinic crystals of $CrK_3(C_2O_4)_3.3H_2O$, which transmit a beautiful blue coloured light. They dissolve in 5 parts of water; the solution being green by reflected, but transmitting red light. On evaporation by heat it leaves an amorphous green mass, which, however, on solution again gives the blue crystals.

To obtain the red potash salt, quadroxalate of potash is saturated with chromic hydrate, and evaporated over sulphuric acid. The small red granular crystals that form are soluble in 10 parts of cold

* Chem. Gaz. 1857, 62. † Compt. Rend. 47, 929.

* M′ represents an atom of a monad, and M″ of a dyad metal.

water; on boiling the cherry coloured solution it turns blackish green.

Analogous compounds are known with ammonium, sodium, calcium, barium, lead and silver, and others. There are also triple salts, as, for example, of potassium, calcium, and chromium.

Iron Oxalates. — Ferrous sulphate is almost wholly decomposed by oxalic acid or oxalate of potash, the precipitate consisting of light yellow hydrated ferrous oxalate, $FeC_2O_4.2H_2O$. The same compound is produced when iron is dissolved in oxalic acid, and when solution of ferric oxalate is exposed to sunlight. It requires 4500 parts of cold water, and 3800 of hot, for solution. It dissolves very little in oxalic acid, but in warm hydrochloric and dilute sulphuric acids with facility, and also in boiling oxalate of potash, from which oily drops of a double salt separate.

Ferric oxalate is produced by treating ferric hydrate with a quantity of oxalic acid insufficient to saturate it. It is a yellow powder, insoluble in water, but which dissolves in an excess of oxalic acid, forming a solution which becomes greenish coloured on exposure to light, evolves carbonic acid, and finally deposits all its iron as ferrous oxalate. It is also slowly precipitated when solutions of a ferric salt and an oxalate are mixed in equivalent proportions.

The alkaline binoxalates dissolve ferric oxide, forming soluble double salts. It is this property which renders salts of sorrel useful for dissolving rust and removing iron stains. The potassio-ferric oxalate is also deposited, after the precipitation of ferric oxalate, from the mixed solution of ferric chloride and neutral oxalate of potash (BUSSY). It dissolves in 14 parts of cold and 4 parts of boiling water. The double sodium salt is even more soluble, requiring only 2 parts of water at 20° C., and two-thirds its weight of boiling water.

There are also soluble double ferric salts with calcium, barium, and strontium, which are formed when it is attempted to precipitate them from solutions containing ferric salts. The oxalates of nickel and cobalt resemble those of iron in their mode of formation and in general properties.

Aluminium Oxalate is obtained as an amorphous transparent mass on evaporation of solution of alumina in oxalic acid. It is deliquescent, swells up when heated, and forms with the alkalies and alkaline earths several double oxalates. Its solution gives no precipitate with calcium chloride.

Stannous Oxalate (SnC_2O_4).—Metallic tin is but little attacked by aqueous oxalic acid, but stannous acetate precipitated with boiling oxalic acid gives a shining crystalline powder of the above composition, insoluble in water, oxalic acid, and but little in dilute mineral acids in the cold. Forms double salts with potash, soda, and ammonia, containing one atom of crystallization water. A solution of stannic hydrate (formed by precipitating stannic chloride with sodium sulphate) in oxalic acid has the curious property of becoming blue in sunlight, and colourless again in the dark.

Bismuth Oxalate, $(Bi_2(C_2O_4)_3.15H_2O$, is a white crystalline precipitate obtained by adding oxalic acid in excess to solution of nitrate of bismuth. It retains 2 atoms of water when dried at 100° C.

Copper Oxalate, $(CuC_2O_4)_2H_2O$, is the precipitate obtained from solution of copper sulphate on addition of oxalic acid. It forms soluble double salts with the alkaline oxalates.

Lead Oxalate (PbC_2O_4) is precipitated by adding oxalic acid to a soluble lead salt. It is insoluble in water and acetic acid, soluble in nitric acid, and in chloride and nitrate of ammonium; not soluble in ammonia or carbonate of ammonia.

Mercurous Oxalate ($Hg_2C_2O_4$) can only be obtained anhydrous by heating the mercuric salt to 164° C. It decomposes at 175°. Obtained by heating mercurous nitrate or oxide with oxalic acid in excess, it is a white precipitate which obstinately retains water, and is decomposed at 100°. The mercuric oxalate (HgC_2O_4) is a white amorphous powder obtained by precipitating mercuric nitrate, or digesting yellow oxide of mercury with excess of oxalic acid. It detonates violently when dry and subjected to friction.

Silver Oxalate ($Ag_2C_2O_4$) is precipitated from solution of nitrate of silver by oxalic acid. Forms small crystals slightly soluble in water, especially on heating; but insoluble in alcohol and ether. It decomposes between 110° and 150°, and detonates when suddenly heated.

Methyl Oxalate, $(CH_3)_2C_2O_4$, is obtained by distilling a mixture of equal weights of sulphuric acid, oxalic acid, and wood spirit; or by digesting equal parts of binoxalate of potash, sulphuric acid, and wood spirit, for several days at the ordinary temperature, and then distilling. Towards the end, pure oxalate of methyl comes over and crystallizes in the neck of the retort; while the first portions, containing unacted-on methyl alcohol, yield crystals of the same on evaporation. It forms beautiful large, tabular crystals, belonging to the rhombic system, transparent, melting at 51°, and boiling at 151°. The aqueous solution decomposes into oxalic acid and methyl alcohol. With aqueous ammonia, the crystals give oxamide. Pure methylic alcohol is best prepared by decomposing this compound, which can easily be obtained pure in consequence of the facility with which it crystallizes.

Ethyl Oxalate, $(C_2H_5)_2C_2O_4$, is a liquid body, boiling at 183° to 184° C., produced by digesting at a boiling heat perfectly anhydrous alcohol with dehydrated oxalic acid in a vessel provided with a vertical condenser, from which the condensed alcohol falls back upon the acid. On distillation, first unacted-upon alcohol comes over, then ethyl formate, and finally ethyl oxalate. It may also be prepared by passing hydrochloric acid gas through a solution of 1 part of dry oxalic acid in 2 parts of absolute alcohol. It is not much dissolved by water.

In addition to the neutral oxalic ethers, there is another series, corresponding to the binoxalates. The monethyl oxalate, or ethyl oxalic acid, as it may be called, is produced by adding 1 molecule of potash in alcoholic solution to 1 molecule of ethyl

oxalate, with vigorous shaking. The potassium ethyl oxalate, a salt insoluble in alcohol, separates in small crystals. The reaction is represented by this equation :—

Ethyl Oxalate. Potash. Potassium Ethyl Oxalate. Alcohol.

$$(C_2H_5)_2C_2O_4 + KHO = C_2H_5.K.C_2O_4 + C_2H_5.HO.$$

A certain amount of oxalate of potash is formed at the same time. To separate the pure compound, the crystals are treated with 80 per cent. spirit, which dissolves the ethyl oxalate of potash; an equivalent of sulphuric acid is added, the separated sulphate of potash filtered off, and the acid liquid neutralized with barium carbonate, and the barium salt obtained crystallized by evaporation on the water bath. The free acid obtained by treating this with the exact amount of sulphuric acid is an unstable body, decomposing on concentration. The salts also, when boiled with excess of alkali, decompose into oxalate of ethyl and oxalic acid.

Manufacture. — The extraction of oxalic acid, as binoxalate of potash, from plants was formerly carried on in Germany as a manufacturing operation, chiefly in Suabia. The plant first employed was the wood sorrel; but the common sorrel giving a larger produce, was afterwards cultivated in fields for this purpose. It was sown in the month of March, and cut down in June. The leaves were beaten in large wooden mortars, and when the mass had assumed the consistence of a paste, it was transferred to tanks, and sufficient water added to render it fluid. After standing five or six days, the whole was filtered, the residue submitted to pressure, and again treated with water. The different liquors thus obtained were run into tanks, and clarified by addition of a small amount of China clay. The clear solution was then decanted, and evaporated in copper pans till a pellicle formed on the surface, when the liquor was run into glazed stoneware coolers to crystallize. A crop of binoxalate of potash was thus obtained, which by re-crystallization was freed from colouring matter. The *Rumex acetosa* yielded ·764 per cent. of the salt (Bannach), and the *Oxalis acetosella* only ·255 per cent. (Savary).

The next process that was adopted for the manufacture of oxalic acid was founded upon Bergman's method of obtaining it by the action upon sugar of nitric acid. As it is now entirely superseded by the process described further on, we shall only give a short account of the process and its various modifications, as interesting from an historic point of view.

Coarse refuse sugars and treacle were treated in earthenware jars, or in closed wooden tanks lined with lead, with nitric acid of specific gravity between 1·200 and 1·270, the temperature being maintained at about 125° Fahr. by means of steam pipes. If the nitric acid were too strong, either formic acid or carbonic acid would be formed. The reaction was found to take place better in presence of the mother liquors of previous operations, and by this means a much larger yield was obtained. The reaction takes place approximately according to the following equation :—

Sugar. Oxalic Acid.

$$C_{12}H_{22}O_{11} + 18O = 6C_2H_2O_4 + 5H_2O.$$

The addition of sugar and nitric acid was continued until the liquid was sufficiently strong to deposit a copious crop of oxalic acid crystals on cooling. One cwt. of sugar yields, under favourable conditions, about 140 lbs., and 1 cwt. of treacle about 116 lbs. of the crystallized acid. Several patents were taken out for the use, in the above process, of other materials than sugar. Nyren converted potato starch and horse-chestnuts, and Rawson, rice, into saccharine matter by heating with dilute sulphuric acid. These improvements appear to have met with little success; but the great waste of the nitrous compounds disengaged, which is the obvious defect of the process, induced many to try, and with better success, to improve that part, and find some plan of saving or utilizing the nitrous gas. It was found impossible to use the gases directly for the manufacture of sulphuric acid, mixed as they were with carbonic acid, which appears to exert a directly detrimental influence in the sulphuric acid chambers. But after absorption of the gases in oil of vitriol, the nitrous sulphuric acid obtained was used instead of nitrate of soda. Jullion converted them back again into nitric acid by passing the gases mixed with air over heated platinum or platinized asbestos, and absorption by water. He subsequently devised another process, working continuously, founded upon similar principles, in which a current of chlorine was employed to oxidise the nitrous fumes. Firmin, to effect the same object, pumped air directly into the oxidising sugar mixture. But, these ingenious devices notwithstanding, the process involved very considerable loss of nitric acid, and was eventually given up in favour of the process now employed, which is next described.

It is founded upon the observation made by Gay Lussac in 1829, that many neutral organic bodies—starch, woody fibre, and the like—when heated with excess of potash or soda, are more or less converted into oxalate of the alkali. This reaction, after remaining almost unnoticed for many years, was taken up by Possoz,* who studied the relative action of the two alkalies, potash and soda, and also determined the yield of oxalic acid that was afforded by various materials when subjected to the process.

The method adopted by Possoz in his researches was to evaporate a caustic lye till the boiling point rose to 225° C. (437° Fahr.), cool it to 180° C. (356° Fahr.), then introduce the starch or meal in small quantities at a time, and expose the mixture to a temperature between 200° to 225° C. (392° to 437° Fahr.) for four hours. With woody matter a somewhat different treatment was adopted. The material was mixed with lye of 1·5 specific gravity (48° Beaumé), the mixture then evaporated or dried, and the remainder of the process conducted as before. The drying with the caustic lye changes the woody fibre into a brown humus-like mass, which, on further heating to 200° to 225° C., becomes first yellow,

* Comptes Rendus, tom. 47, 1858, pp. 207 and 648.

and afterwards white; and after four or five hours' heating contains oxalates, formates, and carbonates in considerable proportions. By conducting the operation at a higher temperature, the change can be more quickly completed; but, at the same time, more or less of the oxalic acid will be destroyed and lost.

The results of a series of experiments conducted in the above manner is given in the following table. Three hundred parts of caustic potash were used with 100 parts of each of the substances named, which had previously been dried as far as possible at 100° C.

	Crystallized Oxalic Acid. Parts.
100 parts of potato starch gave	125
" sawdust "	70
" wheat straw "	100
" hay "	140
" clover "	110
" lucerne "	110
" tansy "	130
" mugwort "	115
" wild chicory "	120
" borage "	112
" nettles "	100
" tobacco stems "	150
" wheaten bran "	150
" woollen rags "	10
" silk rags "	12
" leather "	6
" horn "	20

When soda is substituted for potash the reaction is not the same. The first part of the operation, in which the alkali dissolves the organic matter, gives a similar result to potash, for there is found about an equal quantity of ulmic acid; but upon continuing to heat the mass the oxalic, acetic, and formic acids appear to decompose one another as they are formed, for they are actually present during the whole time. But at whatever period the operation be interrupted, and whatever proportion of soda be employed, only comparatively small quantities of oxalate are formed—ten times less on the average than with potash; while sometimes only traces, and with some substances, wool, silk, leather, not even traces, are to be found. There is also much greater difficulty in working with soda upon a large scale, the yield getting less as the scale of operations increases.

It is not very clear to what this remarkable difference in the action of the two alkalies is to be ascribed. WARD has suggested that potash has a greater solvent action on cellulose than soda; but that this assumption is incorrect will be easily seen when we consider that this great difference is also exhibited when starch is operated upon, and that, as mentioned above, both alkalies first attack and dissolve the cellulose equally; but that with potash the reaction proceeds only to the stage of oxalic acid, while with soda the reaction, indirectly or directly, goes further to the formation of carbonic acid. The explanation offered by POSSOZ is at least in accordance with the ascertained facts. He attributed the destructive action of the soda to its higher melting point, and made experiments which at once gave some countenance to this idea, and pointed out a means of manufacturing the acid with only a limited use of the more costly alkali, potash. When the hydrates of potassium and sodium are mixed the resulting mixture has a fusion point lower than would be expected from that of its constituents, and accordingly, if the explanation offered were correct, the yield of acid with a mixture of the alkalies ought to be equal, if not superior, to that with potash alone. The result of a series of experiments upon starch showed that a mixture of—

Soda.	Potash.	
1 part and	3 parts gave	$\frac{1}{10}$ more than potash alone.
1 "	2 "	$\frac{1}{8}$ " "
1 "	1 part gave	same as potash.
2 parts and	1 "	$\frac{1}{10}$ less than potash.
3 "	1 "	$\frac{1}{5}$ less than potash.

—thus fully bearing out the theory. But notwithstanding this success, POSSOZ, having regard to the greater cost of potash and the facility with which lyes of caustic soda could be obtained in the alkali manufactories, still proposed to use soda alone at the expense of a large proportion of the oxalic acid. On making experiments he found that, by employing a large excess of soda, five or six times the weight of the bran used, and conducting the process at a temperature of 150° to 180° C., he obtained on the small scale a yield of 90 per cent. on the bran used, of the crystallized acid, and on the large scale only 50 per cent. On referring to the table given above it will be seen that, with three times its weight of potash, wheaten bran gives 150 per cent. POSSOZ also observed that the oxalate of soda produced readily separated from the mother liquor (specific gravity 1·32 = 35° Beaumé) on lixiviation of the melted mass. He does not appear to have remembered that this sparing solubility of the oxalate of soda would have an important effect in the use of mixtures of the alkalies, enabling the whole or greater part of the potash to be recovered, as, according to a well-known and pretty general law, first enunciated by BERTHOLLET, there is a great tendency in a mixture to form those compounds which are least soluble.

The conditions under which oxalic acid is formed from sawdust and other materials have recently been further investigated by THORN.* Using fir-tree sawdust with 15 per cent. of hygroscopic water, he mixed it with boiling lyes of from 30° to 42° Beaumé, and further heated it in a shallow iron vessel over an open fire, keeping it well stirred. The lye should not be so strong as to be entirely sucked up by the sawdust, otherwise it cannot be well mixed. Different results were obtained, when the mass was heated in thicker or thinner layers, and another series of experiments was accordingly made, in which the mixture was heated in layers about half an inch thick on flat iron plates. The results, given below, are stated in parts of crystallized acid obtained from 100 of sawdust.

1. With caustic soda alone. One part of sawdust to two parts NaHO treated as above, gave—

* Dingler's Journal, 210, p. 24.

Temperature.	Thick Layers.	Thin Layers.
200° C.	36 parts acid	34·68 parts
220°	—	31·6 "
240°	33·2 parts acid	—

By doubling the proportion of NaHO, the yield was increased to 42·3 in thick and 52·14 in thin layers, the temperature being finally raised to 240°. Great care has to be used in heating above 200°, or overheating will occur and some oxalic acid be destroyed.

2. With mixed potash and soda. When 1 part sawdust is heated with a mixture containing 10 per cent. of KHO, a peculiar and characteristic decomposition ensues. By either quick or gentle heating (in thick layers) the mass turns greenish yellow, and becomes a thick pasty mass as the temperature rises to 180° C. A cloud then appears over the mass; the temperature, after removing the source of heat, rises by itself, first slowly, then within a minute to above 360°, the mixture swells up, evolves large quantities of inflammable gas, and finally becomes carbonized. This destruction always occurs with the above proportions, and cannot be arrested by cooling the hot mass by blowing a strong current of cold air upon it. With a mixture containing 20 per cent. of KHO the same reaction does not occur.

The following table shows the result of heating sawdust with double its weight of mixed alkalies for one hour:—

Percentage of KHO in the Alkali.	Thick Layers.		Thin Layers.	
	Temperature.	Yield.	Temperature.	Yield.
	Degrees C.		Degrees C.	
0	240	33·2	200–220	33·14
10	—	—	230	58·36
20	190	19·78	—	—
"	200	21·50	—	—
"	240	30·04	240–250	74·76
30	190	21·38	—	—
"	240	38·89	240–250	76·77
40	190	14·00	—	—
"	200	30·35	—	—
"	240–245	43·70	240–250	80·57
50	200	25·76	—	—
"	240–245	39·04	—	—
60	200	30·57	—	—
"	240–245	42·67	240–250	80·08
80	200–220	45·59	—	—
"	240	61·32	245	81·24
90	240	64·24	—	—
100	240–245	65·51	240–250	81·23

It will be noticed that these results do not agree entirely with those of Possoz. The method, however, was somewhat different, and the experiments of Possoz with the mixed alkalies were made upon starch, and not sawdust. The results of heating in thin layers, given in the above table, show, however, that even with sawdust an alkali containing 40 per cent. KHO gives a yield approximately equal to that with pure potash. It will also be seen that the experiments with thin layers show a remarkable increase in the percentage of oxalic acid, due perhaps to the increased surface exposed to the air, which at once facilitates the drying and the oxidation of the organic matter, and thus allows the operation to be conducted without fusing the mass. Experiments were made to ascertain whether a current of hot air aided the formation of oxalate. It was found not to do so. With different kinds of sawdust it was found that a larger yield was obtained from soft woods—fir, pine, poplar—than from hard wood, such as oak and beech; and it was also determined by quantitative experiments, that a greater proportion than one of sawdust to two of alkali could not be advantageously employed.

The details of the process, founded upon the above facts, that is actually employed in the manufactories are variously stated by different authorities; and as the manufacturers very jealously keep their particular processes secret, it is impossible to give authoritatively the exact method of procedure, or the proportions employed. It is possible, however, to give a general account of the several processes employed, partly from patents taken out in this country, and partly from information which from time to time has appeared abroad, which, though not exactly agreeing with that adopted by any one manufacturer, still give an accurate idea of the manufacture.

Sawdust appears to be the material always employed. It is mixed with a more or less causticized alkaline lye of about 1·35 specific gravity (38° Beaumé), in the proportion of 1 part to 2 or 3 of the alkalies. The proportion of potash to soda used is variously given. FLECK gives 3 parts KHO to 2 parts NaHO, as the proportions employed by ROBERTS, DALE, & Co. (who first applied and patented the process in this country), while others say about equal weights are employed by the same firm. In another place 1 part of KHO to 2NaHO; and in still another, 1 part of KHO to $1\frac{1}{2}$ of NaHO are recommended; while KUHNHEIM in Berlin actually employs equal weights. A more recent patent of DALE'S directs that the sawdust be first treated with an alkaline ley, by which it is freed from resinous and other matters, leaving a purer cellulose behind, which gives a better product than the raw sawdust.

The mixture, which must be well incorporated, is then spread in a thin layer upon iron plates heated by flues underneath, the air being allowed freely to play over the surface. It quickly becomes dry, and the temperature must then be very nicely managed, and kept as nearly as possible at about 200° C., or between that and 225° C., until the sawdust has disappeared and the mixture become white; the greatest care being taken to avoid over-heating, which, though causing the quicker disappearance of the sawdust, would occasion great loss of oxalic acid. The process lasts about six hours.

There is a modified process for converting the sawdust, in which lime is employed in addition to the alkalies. The lime is slaked with the alkaline lye, mixed intimately with the sawdust, and heated on the bed of a reverberatory furnace to a temperature under 250° C. To obtain good results it is necessary that the mass should be evenly heated throughout, and to effect this the mixture must be frequently raked over, and the heating very nicely

managed. The proportions employed are kept secret. There is obtained as product a mass rendered porous by the lime, and consisting chiefly of oxalate of lime and carbonates of potash and soda, upon lixiviating which the latter dissolve out, leaving only oxalate and carbonate of lime. It is said that in this way, by again causticizing, it is possible to employ the same alkali over and over again with but a small percentage of loss. The oxalate of lime, when washed free from alkalies, can then be decomposed with sulphuric acid, as described further on.

The product of the former process, consisting of oxalate of soda, carbonate of potash, humus, and the excess of alkali, may be dealt with in several ways to obtain the acid. By systematic treatment with the smallest possible quantity of cold water, taking care that the liquid running through is not weaker than 35° Beaumé, the oxalate of sodium remains, only a small quantity going into solution; but, according to THORN, there is still a considerable amount of oxalic acid in the liquor, existing no doubt as oxalate of potash. The adhering liquor is removed by washing with cold water till the washings have a specific gravity of 1·03.

By another method, the mass is dissolved altogether by boiling, in the smallest possible quantity of hot water, the liquor concentrated to 38° B. (1·35 specific gravity), and allowed to cool. The oxalate of soda then crystallizes out. If too small a proportion of alkali to wood has been employed in the previous operation, the mother liquor will contain humus-like matters, and be very dirty, thick, and difficult to separate from the sandy deposit of oxalate of soda; and, moreover, the latter will remain partly in solution; but with proper proportions and due concentration it is possible to get a mother liquor free from oxalic acid. This mother liquor is causticized, a quantity of caustic soda added corresponding to that removed as oxalate, and used again for converting another quantity of sawdust. It will then contain too much organic matter to be again employed, without being previously evaporated and calcined to purify it. The oxalate of soda obtained by either of these processes, being freed as completely as possible from adhering mother liquor, is next converted into oxalate of lime, by boiling its solution for one or two hours with a slight excess of milk of lime, having the solution somewhat dilute, otherwise a larger excess of lime must be used, and the reaction will take longer time to complete; which may be known to be the case when a sample of the liquid, after filtration and addition of acetic acid in excess, gives no precipitate or cloudiness with chloride of calcium. The reaction is represented by this equation:—

$$CaH_2O_2 + Na_2C_2O_4 = CaC_2O_4 + 2NaHO.$$

The soda is obtained as a caustic lye, and may be used again in the process after due concentration. The oxalate of lime precipitate, after separation from the soda solution, is boiled once with water and filtered off.

It has been proposed to boil the melted product from the sawdust directly with quick-lime; but by so doing the oxalate of lime is obtained mixed in large proportion with carbonate, giving a larger precipitate to deal with, and thus necessitating larger vessels, besides wasting a quantity of sulphuric acid in its subsequent treatment.

To obtain the oxalic acid from the lime salt resulting from any of the above processes, it is treated in large lead-lined wooden vats with sulphuric acid. It is found necessary for complete decomposition to employ, not merely sufficient sulphuric acid to saturate the lime, but a large excess, 3 equivalents to every equivalent of the oxalate of lime, and not only that, but to employ a large bulk of water in addition. The precipitate is mixed to a thin cream with water, the requisite quantity of acid of 15° to 20° Beaumé added, and well agitated. It will become moderately stiff from formation of gypsum, but after standing, turns thinner again; water is added sufficient to again make a thin cream, and the whole well stirred and boiled for one or two hours until a sample of the precipitate, after washing and treating with acid, shows no oxalic acid when tested with permanganate of potash. The acid fluid, partly decanted and partly filtered from the gypsum, is concentrated to 15° Beaumé (1·116 specific gravity), when some gypsum separates, and then further evaporated to 30° Beaumé (1·261 specific gravity), and allowed to cool, when the oxalic acid crystallizes out in long crystals. The mother liquor, from which the greater part of the oxalic acid has in this manner been removed, is employed again to act upon a fresh quantity of oxalate of lime; and so on until it contains too much organic matter, and becomes too dirty to give a pure acid. It is then concentrated; the organic matter becomes destroyed and oxidised at the expense of part of the sulphuric acid, the bulk of which is obtained pure enough to use again. The washings of the gypsum are used to dilute the sulphuric acid for operating on another quantity of oxalate of lime. The great object of the manufacturer in conducting this process is to lose as little alkali as possible. The method employed to regenerate the alkalies is thus of great importance from an economic point of view. It is found impossible to carry the heating with sawdust so far as to destroy all the humus substances which are first formed, and not transformed into oxalic acid; and accordingly when the product is lixiviated these pass into solution with the excess of alkali, and remain in the mother liquors. If, then, these liquors were merely recausticized and used again, they would acquire a fresh quantity, and after a few operations become so rich in organic matter as not only to give an impure oxalate of soda, but be exceedingly difficult to work with. To purify them they must be concentrated to 40° Beaumé (1·38 specific gravity), mixed with as much sawdust as will completely absorb them, and roasted at a high temperature, either on iron plates heated by a fire underneath, or on the bed of a reverberatory furnace. The product is a mixture chiefly of carbon with carbonated and

caustic alkali, is of a greyish-black colour, very porous, and easy to lixiviate. The solution obtained from it is free from organic matter, and after separation from insoluble residue is causticized with milk of lime, concentrated to 42° Beaumé (1·407 specific gravity), and used again. If evaporated without this addition of sawdust the residue would be easily fusible, and impossible to calcine thoroughly.

The oxalic acid having been obtained, if the mother liquor were clean and free from alkali, may be white enough and pure enough to send into the market; but if not, the greater part of the adhering mother liquor is separated in a centrifugal dryer lined with lead, and the crystals, which will contain sulphuric acid and acid oxalates of soda and potash, besides colouring matter, treated for purification by washing away the remaining mother liquor with a small quantity of cold water, and re-crystallizing from the smallest possible amount of boiling water. As the acid oxalates of the alkalies are less soluble than oxalic acid, it is impossible to remove them, if present in any considerable proportion, by crystallization in the usual manner. To purify oxalic acid contaminated with alkali, it must be re-crystallized from hydrochloric acid of 10 to 15 per cent., which keeps the alkali in solution as chloride; and the crop then obtained, after being washed, must be re-crystallized from water to separate adhering hydrochloric acid. It is not, however, necessary for the purposes of commerce to purify the acid further than by washing away mother liquor, or once re-crystallizing it, to free it from sulphuric acid and colouring matter.

Uses.—Oxalic acid is not the staple material of consumption in any great industry or manufacture, but it is nevertheless very extensively employed for auxiliary purposes in many of the arts.

The chief consumers of the acid are dyers and calico printers, who employ it for many different purposes in their operations. Among other things, they use it in conjunction with other acids as a "discharge," to produce white patterns on a coloured ground. For this purpose, the acids are mixed into a paste with starch or British gum, and printed upon the cloth, which is then passed through a dilute solution of chloride of lime, kept alkaline by addition of lime or chalk. Wherever the acids are printed on the ground, chlorine is liberated, and the colour at the place bleached, or, as it is termed, "discharged." The following two recipes for discharges will give a general idea of their nature:—For further illustrations the reader is referred to the article Dyeing and Calico Printing.

Discharge for Madder Blue.	
Oxalic acid,	2 lb.
Oil of vitriol,	7½ fl. ozs.
British gum,	2 lbs.
Flour,	2 lbs.
Water,	1 gallon.

Discharge for Indigo Green.	
Oxalic acid,	½ lb.
Tartaric acid,	5 lbs.
Starch,	3 lbs.
Water,	3 quarts.

There is also another analogous end for which oxalic acid is employed by the dyers, namely, as a "resist," or chemical "reserve." For this purpose the oxalic and citric acid mixture is printed on the cloth before mordanting, and prevents the absorption of iron and alumina by the fabric when the piece comes to be immersed in the mordant bath. Subsequently, when treated in the dye vat, those parts where the acid has been applied, and where consequently there is no mordant, will not fix any colour. The action is due in part to the fact, that soluble oxalates and citrates of iron and alumina are formed, and in part to the protective action of the gelatinous matter with which the oxalic acid is applied.

Dyers also use oxalic acid in the dye vats, as a constituent in the formulæ employed for many colours, both for cotton, wool, and silk.

It is used by curriers for whitening leathers, as for breeches and boot-tops; and by marble masons for removing iron stains from their work.

In the manufacture of leghorn hats and straw bonnets, it is employed for bleaching and whitening the straw.

For domestic purposes oxalic acid is frequently employed, as for removing ink stains and iron mould from linen, wood, &c., and for scouring boards, which it renders very white, while scrubbing with soap or soda gives an objectionable dirty grey tint. Boards so blackened are restored by washing with a solution of oxalic acid, containing about half an ounce to a quart of water. It is also employed both in the household and in the arts, for cleaning brasses and scouring rusty or tarnished metals, being much better adapted for this purpose than the very corrosive and destructive oil of vitriol which is often used, while its expense is but very little more. In 1851 it used to cost (wholesale) 15*d.* to 16*d.* per lb.; while in 1867, after the introduction of the manufacture by alkalies, it fell to 8*d.* to 9*d.*, and since then has gradually fallen to about 5*d.* a lb., its present price (1877).

There is a considerable demand for it for miscellaneous uses in many small trades and manufactures—mostly analogous to those above mentioned.

The acid oxalate of potash ($KHC_2O_4.H_2O$) is used as a weak acid for scouring metals, and for domestic purposes is sometimes employed, instead of the acid, for removing ink stains and iron mould from linen, the fibre of which it does not damage, while it forms with the iron a double salt soluble in water, and hence washing away.

Oxalic acid has no corrosive action upon vegetable fibres, yet it is sufficiently strong an acid to do all that even the most powerful mineral acids can effect. Hence it is used for many purposes where the use of mineral acids is precluded by the destructive manner in which they affect organic matter.

Detection.—Among organic bodies oxalic acid is peculiar in not giving any carbonaceous residue when it or its compounds are subjected to the destructive action of heat. When the free acid is heated it volatilizes without residue, giving off acid fumes, and the salts decompose, evolving gaseous products, and leaving carbonates of the fixed base in the case of the alkalies and earths; but oxides in the case of the metals, and even the metals themselves when these are easily reducible, as with mercury and silver.

Heated in the solid state with concentrated sulphuric acid, oxalates, as well as the acid, evolve gas, a mixture of equal volumes of carbonic oxide and carbonic acid, the former of which may be recognized by its combustibility, while the latter will give a precipitate with lime water. The method of applying the test is to heat with the sulphuric acid in a test tube, loosely closed with the finger, and apply a light. If the gas burns, it is probably carbonic oxide. The flame is extinguished, and the gas as it comes off is poured into another test tube, containing a little lime water. If on shaking up a precipitate is produced, it indicates the presence of carbonic acid in the gas. The two indications furnish a good clue to the presence of oxalic acid, which is rendered almost a certainty if the substance does not effervesce with nitric or hydrochloric acids, and gives a white, finely-pulverulent precipitate with both calcium chloride, lime water, and calcium sulphate, insoluble in acetic and oxalic acids, readily soluble in nitric and hydrochloric.

The solution (either in water or acid), when mixed with permanganate of potash and acidified, destroys its magnificent red tint, at the same time effervescing from the escape of carbonic acid; and when the solid body, mixed with black oxide of manganese, is treated with diluted sulphuric acid, an effervescence of the same gas will also be noticed.

ESTIMATION.—1. *As Carbonate of Lime.*—The solution, freed, if necessary, from carbonates by boiling with a slight excess of hydrochloric acid, is either neutralized or rendered slightly acid with acetic acid by adding sodium acetate. A sufficiency of acetate of lime is then added, and the fine precipitate of oxalate of lime allowed to subside. The supernatant fluid is decanted through a filter, and the precipitate washed on to it with hot water, taking care to allow each portion to pass completely through before adding more. After washing completely, the precipitate is ignited in a platinum crucible to bare redness, the filter ash added, and the carbonate of lime, resulting from decomposition of the oxalate, weighed. If too strongly ignited, the residue will show a strong alkaline reaction when moistened and placed upon litmus paper. It must be washed into the crucible, moistened with carbonate of ammonia solution, again gently ignited, and re-weighed. One part of carbonate of lime corresponds to 1·26 part of crystallized oxalic acid, or ·88 part of C_2O_4. The solution must not contain magnesium salts in quantity, or manganese, iron, chromium, aluminium, copper, or any heavy metal. (*Vide Oxalate of Lime, ante*).

2. *As Oxalate of Lime.*—The solution must be precipitated, &c., as above directed; but collected upon a weighed filter, which is then dried and heated on the water bath till its weight is constant. The gain in weight of the filter will give the amount of $CaC_2O_4.H_2O$, each part of which represents 1·0678 part of crystallized oxalic acid, and ·7457 of C_2O_4.

3. *By Standard Potassium Permanganate.*—A solution of permanganate of potash is made of convenient strength, 100 c.c., about equal to ·1 or ·2 gram. of crystallized oxalic—either air-dried oxalic acid, sublimed oxalic acid, or crystallized ammonium oxalate being used to standardize it. The solution of the oxalate, which must be free from sulphites, hyposulphites, sulphides, and organic matter, or any other reducing agent besides oxalic acid, is strongly acidulated with sulphuric acid, and warmed to 60° C. The solution of permanganate is then run in, well stirring all the time, until the fluid shows a pale rose tint, permanent for five minutes. The end of the reaction is very abrupt and sharp, there being considerable risk of overrunning the mark if the permanganate is added too hastily. The decomposition is represented by the equation—

$$K_2Mn_2O_8 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

The carbonic acid escapes with effervescence.

Hydrochloric acid and chloride must be absent from the liquid, or the results will be too light, owing to partial oxidation of the hydrochloric to hypochlorous acid or free chlorine. To insure this the permanganate solution must be prepared from the crystallized salt, and not from the commercial solution or rough manganate, which contain much potassium chloride.

4 *As Carbonic Acid.*—When black oxide of manganese in fine powder is mixed with an oxalate, and treated with diluted sulphuric acid, the oxalic acid is oxidised, at the expense of the excess of oxygen of the peroxide, to carbonic acid, which escapes, while manganese goes into solution as manganous sulphate, according to the equation:—

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2.$$

When this reaction is performed with weighed materials in a weighed apparatus, which will dry the escaping gas, the loss in weight will represent carbonic acid. For a drawing and description of the apparatus of FRESENIUS and WILL, and the method of conducting the operation with manganese, see article CHLORINE. The peroxide of manganese must be free from carbonates, and care must be taken cautiously to remove *all* the carbonic acid from the apparatus before reweighing it. Other oxidising bodies may be substituted for the manganese, as chromate or bichromate of potash, peroxide of lead, and other peroxides. Free oxalic acid must be neutralized with alkali before adding it to the oxidising agent, or carbonic acid will be formed before the apparatus can be weighed.

The loss in weight multiplied by 1·4318 will give the amount of crystallized oxalic acid, and will, of course, be itself the weight of C_2O_4 in the quantity taken.

5. *As Metallic Gold.*—The solution of the oxalate in water, or in the smallest possible amount of hydrochloric acid, is largely diluted and boiled for some time with solution of ammonio or sodio-terchloride of gold, avoiding direct exposure to light. The precipitated gold, after subsidence in the dark, is collected, washed, ignited, and weighed. The reaction is according to the equation—

$$2AuCl_3 + 3H_2C_2O_4 = 6CO_2 + 6HCl + Au_2.$$

From which it is evident that every part of gold is equivalent to ·957 parts crystallized oxalic acid, or to ·4456 of C_2O_4. This method is used when it is desired to estimate the oxalic acid and the bases in the same portion of substance. The excess of gold in the filtrate may be separated by sulphurous acid, or addition of oxalic acid in slight excess.

6. Oxalates and oxalic acid may also be estimated by burning with oxide of copper in the usual way of organic combustion analysis.

OXYGEN.—*Oxygène*, French; *Sauerstoff*, German. Atomic weight, 16. Symbol, O.—This gas is the most abundant of all the elements. It forms a principal part of the earth's surface, inasmuch as eight-ninths of the water and about one-half of the chalk, alumina, and silica, by weight, are oxygen. It also constitutes one-fourth of the atmosphere. Specific gravity 1·1056 (air = 1).

Oxygen was discovered by PRIESTLEY in 1774. Its properties are so well known that it is only necessary here to give the various modes of making it.

A large number of the oxides, when heated, part with more or less of their oxygen, being reduced either to the metallic state or to lower oxides. Thus mercuric oxide, HgO, when strongly heated splits into Hg + O.

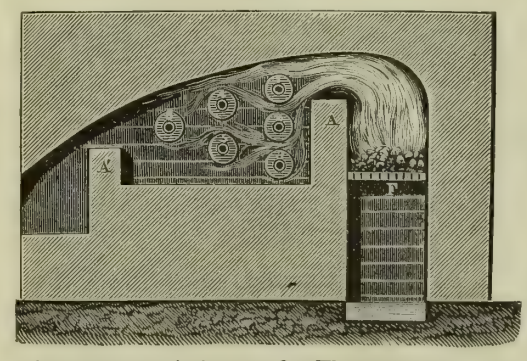
Manganese dioxide, when reduced to powder and heated to redness, passes into manganic oxide with evolution of oxygen—

$$3MnO_2 = 2O + Mn_3O_4.$$

This reaction is much used for the manufacture of oxygen for the lime light and other purposes: 1 gram. of manganese dioxide yields 0·034 gram. or 24 cubic centimétres of oxygen, while 1 gram. of the hydrated dioxide yields 0·3 gram. or 21 c.c. Therefore, for the production of 1 litre of oxygen 42·37 grams. manganese dioxide, or 47·2 grams. hydrated dioxide, are required.

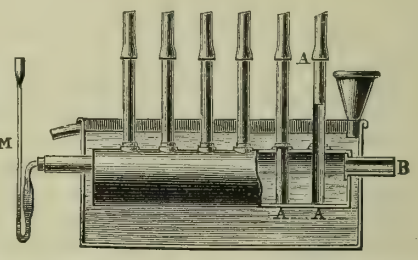
An approved apparatus is shown in the cut, Fig. 1. The vessels used are commonly the iron bottles in

Fig. 1.



which mercury is imported. The engraving shows six such vessels charged with manganese dioxide, and disposed in a reverberatory furnace so as to be exposed to overlapping flames. F is the fire, A the bridge. The gas is collected by iron pipes luted to the bottles and conveyed to the condensing arrangement shown in Fig. 2. This consists of a cylindrical tube into which the pipes, A, from the furnace lead;

Fig. 2.



it is furnished with a manometer, M, at one end; at the other is an outlet, B, leading to the gasholder. The cylinder is surrounded by flowing water, so that the gas may be cooled.

Potassium chlorate when heated to bright redness yields oxygen. In the laboratory this process is commonly used to obtain small quantities of pure gas. The reaction is—

Potassium Chlorate.		Potassium Chloride.		Oxygen.
$KClO_3$	=	KCl	+	O_3.

It has been found that the addition to the potassium chlorate of one-fourth of its weight of manganese dioxide, or black oxide of copper (which do not themselves lose oxygen), causes the decomposition of the former salt at a much lower temperature than when heated alone.

A mixture is made of 4 parts of chlorate of potash with 1 part of powdered black oxide of manganese. In the preparation of this mixture care must be taken to avoid the accidental introduction of small fragments of organic matter. One pound of this mixture, when heated, yields about 4 cubic feet of oxygen; more might be obtained by powdering the crystals, but the process is less safe. A small quantity of the oxygen mixture should be heated in a test tube before using it on a large scale, as occasionally the manganese dioxide contains lamp black and substances of kindred nature, whose presence would lead to an explosion. The residuary manganese may be collected by straining through calico, and can be used *ad infinitum*.

Bleaching powder heated to redness, together with a little slaked lime, gives off oxygen (H. DEVILLE).

A concentrated solution of bleaching powder, when gently heated with a small quantity of cobaltic oxide (Co_2O_3) (0·5 per cent., or less), is completely resolved into chloride of calcium and oxygen. The gas is evolved with great ease and regularity, so that this method is well adapted for the preparation of large quantities. The same cobaltic oxide may be used repeatedly, as it does not undergo any permanent change (FLEITMANN).

BÖTTGER states that cupric oxide and ferric hydrate play the same part with bleaching powder as cobaltic oxide, but that the action is less energetic.

Sulphuric acid, when passed in vapour over red-hot platinum plates or spongy platinum, is decom-

posed into water, oxygen, and sulphurous oxide. The sulphurous oxide is absorbed by water or an alkaline solution, and can be used to manufacture more sulphuric acid. H. DEVILLE and DEBRAY put this forth as the cheapest mode of manufacturing oxygen on a large scale.

Sulphate of zinc, moderately heated, yields oxygen by a like decomposition.

$$ZnSO_4 = ZnO + SO_2 + O.$$

Oxygen in the air is mechanically mixed, not chemically combined; it can therefore be isolated by physical means. GRAHAM succeeded in obtaining oxygen from the air by dialysis, the membrane used being a sheet of caoutchouc.

MONTMAGNON and DELAIRE make use of charcoal: 100 litres of wood charcoal will, when exposed to the atmosphere, occlude 925 litres of oxygen, but only 705 litres of nitrogen. Now it would appear that when the charcoal thus saturated with gas is placed in water, 650 litres of nitrogen are expelled, but only 350 litres of oxygen. Thus the charcoal now contains 575 litres of oxygen and only 75 litres of nitrogen, which is oxygen practically pure for commercial purposes. To extract the gas a pump is used.

MALLET'S process depends on the different degrees of solubility of oxygen and nitrogen in water. Air is forced into water by means of a forcing pump; and the gases which escape on diminishing the pressure are again subjected to the same treatment several times in succession, until at length nearly pure oxygen is obtained. The table below shows the composition of the artificial air at each successive stage:—

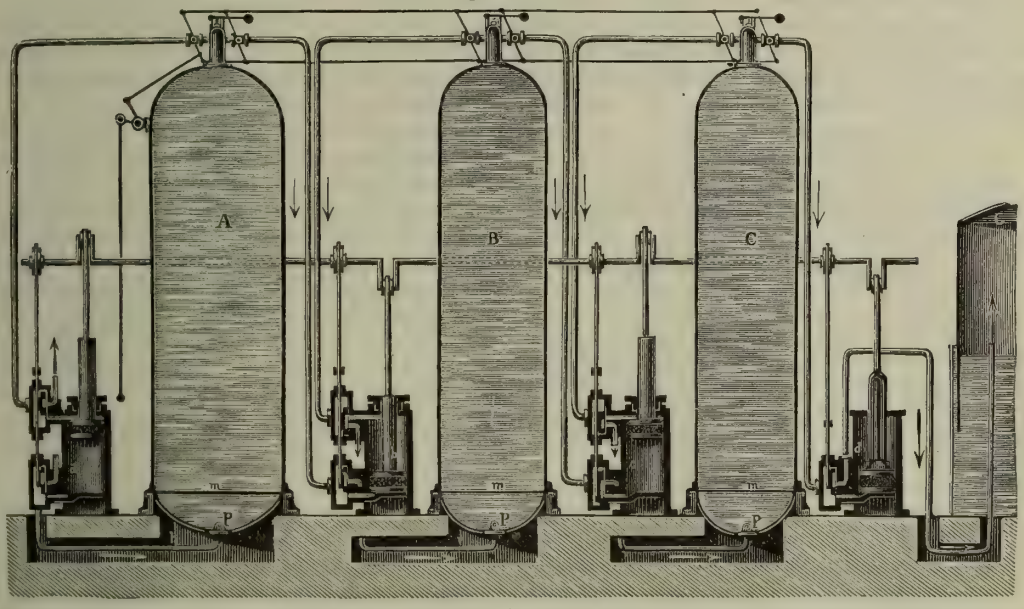
COMPOSITION AFTER SUCCESSIVE PRESSURES.

Air.	1.	2.	3.	4.	5.	6.	7.	8.
N 79,....	66·67	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O 21,....	33·33	47·5	62·5	75·0	85·0	91·0	95·0	97·3

The apparatus, as described by J. PHILLIPS, is shown in Fig. 3.

The first absorption cylinder, A, has a contents of

Fig. 3.



10 cubic mètres; the second, B, of 7 c.m.; the third, C, of 5 c.m. With apparatus of this size, and a pressure of five atmospheres, 773 litres of gas are obtained by each operation.

The pump, *a*, sucks in the outer air, and delivers it by the pipe, *h*, to the lower part of the cylinder, A, through the valve, *p*. The air streams upwards against the plate, *m*, which is pierced with minute holes, and disperses in minute bubbles through the water.

The undissolved part of the air is either allowed to escape through a valve at the top of the cylinder, or is conveyed to the upper part of the air pump to assist the pressure.

The pumps, *b*, *c*, *d*, are worked in precisely the same manner as *a*, except that they draw denitrogenized air from the cylinder behind them. Finally, the air, freed from the greater part of its nitrogen, is forced into the gasholder, G.

As regards the price of the artificial air, containing 50 to 75 per cent. of oxygen, it is stated that this may be prepared on a large scale at a cost of 15 centimes ($2\frac{1}{2}d.$) per cubic mètre (a little more than 35 English cubic feet).

Barium dioxide (peroxide of barium), BaO_2, when heated to redness, yields one-half of its oxygen, producing baryta. ($BaO_2 = BaO + O$). The peroxide is prepared by heating the baryta to a less degree in a current of moist air. On shutting off the air and raising the temperature oxygen is given off, and baryta formed; so that by repetitions of the process indefinite quantities of oxygen may be obtained

with the same quantity of material. If the baryta fuses, it can be revivified by adding to it a little lime, magnesia, and manganate of potassium.

J. A. Wanklyn, observing that copper oxide gave up its oxygen to barium oxide, producing barium dioxide, proposed to utilize this property, in connection with the fact that metallic copper when highly heated becomes oxidised to copper oxide, for the economical production of oxygen from atmospheric air.

The barium oxide is mixed with at least half its weight of copper oxide, placed in an iron retort and heated to redness, a jet of steam being blown in. The barium dioxide at first formed gives up its oxygen and becomes oxide again. Atmospheric air is then blown into the retort (the steam being stopped), which again, through the mediation of the copper oxide, oxidises the baryta to barium dioxide. This is then decomposed by steam as before.

Instead of baryta, caustic lime or manganese dioxide may be used, or a mixture of the latter with lime or baryta.

Cuprous chloride absorbs oxygen from the air, which it again liberates when heated to 400° C. The cuprous chloride is best prepared by heating cupric chloride rather strongly, whereby one half of the chlorine is evolved, and can be utilized in preparing more cupric chloride. The equation is this—

$$2CuCl_2 = Cu_2Cl_2 + 2Cl.$$

The cuprous chloride when moistened and exposed to air absorbs oxygen, with formation of oxychloride of copper, thus—

Cuprous Chloride. Oxychloride of Copper.

$$Cu_2Cl_2 + H_2O + O = CuCl_2,CuO + H_2O.$$

The resulting mass, when heated, first gives off water and then oxygen, leaving cuprous chloride. This taking up and giving off of oxygen may be repeated as often as desired: 100 lbs. of cuprous chloride when heated in this fashion, will yield 50 cubic feet of oxygen at each operation.

To prevent the cupric chloride caking together, it is mixed with 33 per cent. of broken pottery ware. The taking up of oxygen goes on very rapidly even in air at an ordinary temperature, but becomes almost instantaneous in the presence of steam and air at 200° C.

Maréchal and Tessié du Mothay's process has been carried out on a large scale. When permanganate of potassium is heated to redness, it gives off about 10 per cent. of the oxygen which it contains. The operation is facilitated by the passage of a current of superheated steam over the salt. In practice sodium permanganate is used.

The process is carried on in brick furnaces, with the fire-boxes so arranged as not only to heat the retort which holds the sodium permanganate, but also one or more chambers through which the blast passes to the retort.

About 600 lbs. of the salt are placed in the retort, and heated to the requisite degree in the furnace; superheated steam from the boiler is then admitted for about ten minutes, when the following reaction takes place:—

$$2Na_2MnO_4 + H_2O = Mn_2O_3 + 4NaHO + 3O.$$

At the conclusion of this part of the process the steam is shut off, and superheated air is admitted for about fifteen minutes, whereupon the manganic oxide combines with more oxygen, and is reconverted into manganic acid, which of course resumes its former relation with the sodium, and is ready for a repetition of the process.

A steam pumping engine is used for the air blast.

The material can be used continuously for some months without rechanging the retorts. In the works in New York 25,000 cubic feet are produced by the consumption of 2 chaldrons of coke, and with the labour of three men.

OZONE.—English, French, German. Formula, O_3. —Towards the end of the last century Van Marum observed that oxygen gas through which electrical sparks have been passed, acquired a peculiar odour and the property of attacking mercury. For upwards of half a century this observation attracted no attention.

In 1840 ozone was discovered by Schönbein whilst experimenting with Grove's battery on the electrolysis of water. He found that an odorous substance accompanied the oxygen evolved at the positive pole; that this substance may be preserved for a long time in well-closed vessels; and that its production is influenced by the nature of the metal which serves as the pole, by the chemical properties of the electrolytic fluid, and by the temperature of that fluid as well as of the electrode. The same body he found to be produced by holding a strip of platinum or gold near the knob of the prime-conductor of an electrical machine. With great sagacity he recognized the identity of the peculiar odour which accompanies a flash of lightning with that of the new substance which he termed ozone.

Schönbein soon afterwards discovered that ozone is formed when phosphorus oxidises slowly in moist air or oxygen.

To Schönbein then is due the great merit of recognizing ozone as a distinct form of matter, having an identity of its own by whatsoever means prepared, as also the merit of discovering the most important means for the production of ozone, and of establishing its principal properties and reactions.

The general properties of ozone are those of an active oxygenant. Thus, like chlorine and peroxide of nitrogen, it bleaches colouring matters, corrodes fabrics, tarnishes or otherwise attacks metals, and liberates iodine from potassium iodide. Its special properties are its characteristic pungent odour, its destructibility by a moderate heat, and its non-manifestation of any acidulous reaction.

In 1841 Schönbein put forth the view that ozone was an oxide of hydrogen, since it is only in the presence of moisture that air or oxygen when passed over phosphorus produces ozone, and that no ozone can be formed from air, even if moist, which has been deprived of its oxygen.

In 1845 this view was shown by MARIGNAC and DE LA RUE to be incorrect, for in a paper published in the "Archives of Electricity," they established the important fact that ozone is produced by the action of the electric spark upon pure dry oxygen—a point which was further and conclusively demonstrated by the investigations of FREMY and BECQUEREL in 1852, who also discovered that when electric sparks were passed through pure oxygen gas, inclosed in a confined space in contact with a solution of iodide of potassium, or with moistened silver, the oxygen was, after a lapse of sufficient time, totally and completely absorbed by those substances. It was thus proved that for the formation of ozone oxygen alone is required.

The hypothesis of SCHÖNBEIN, however, received some support from an elaborate investigation of BAUMERT ("Poggendorff Annalen," 1853), who maintained that water is always formed when dry ozone, prepared by electrolysis, is destroyed or decomposed by heat. He inferred that two distinct bodies had been confounded under the name of ozone—(1) allotropic oxygen, formed by the passage of the electric spark through oxygen; and (2) a teroxide of hydrogen, produced in the electrolysis of water.

ANDREWS in the same year repeated BAUMERT'S experiments, but failed to find the slightest trace of water; and came to the conclusion that no gaseous compound having the composition of a peroxide of hydrogen is formed during the electrolysis of water; and that ozone, from whatever source derived, is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition.

The next step in the history of ozone was the discovery by ANDREWS and TAIT ("Phil. Trans.," 1860) that oxygen gas in changing into ozone diminishes in volume, or becomes condensed, recovering its original volume when the ozone is changed back into oxygen by the action of heat or otherwise. In the same paper it was shown that no further diminution of volume occurred when the contracted gas was agitated with a solution of potassium iodide, so as to absorb the ozone. A similar result was obtained on agitating the contracted gas with iodine. The ozone reaction in both these cases disappeared, but without causing any change in the volume of the gas.

ANDREWS and TAIT did not attempt to give any absolute explanation of these singular facts; but inferred that, on the allotropic view of the constitution of ozone, its density must be enormously great.

A happy explanation of these experiments was proposed by ODLING in 1861 ("Manual of Chemistry," ODLING, p. 94). "If we consider ozone to be a compound of oxygen with oxygen, and the contraction to be consequent upon their combination, then if one portion of this combined or contracted oxygen were absorbed by the reagent, the other portion would be set free, and by its liberation might expand to the volume of the whole. Thus, if we suppose 3 volumes of oxygen to be condensed by their mutual combination into 2 volumes, then on absorbing one-third of this combined oxygen by mercury, the remaining two-thirds would be set free, and consequently expand to their normal bulk, or 2 volumes—

$$OOO + 2Hg = Hg_2O + OO."$$

SORET, experimenting in 1866 upon the mixture of oxygen and ozone obtained by electrolysis, made the important discovery, that if this mixture is brought into contact with oil of turpentine or oil of cinnamon, a diminution takes place equal in amount to twice the augmentation of volume which the same mixture would sustain if the ozone were converted by heat into ordinary oxygen. In other words, the volume of ozone, measured by its absorption by the essential oil, is twice as great as the difference between the volume of the same ozone and oxygen. SORET'S conclusions were correct; but the data upon which he founded them were very inaccurate, and by no means justified those conclusions.

The study of the quantitative reaction of ozone was carried out by Sir BENJAMIN BRODIE, his papers published in 1872 corroborating and extending the less exact results of SORET, and establishing the correctness of ODLING'S suggestion.

The quantitative reactions of ozone, as elaborated by BRODIE, constitute a body of exact information as to the chemical properties of ozone, through which it is finally removed from the domain of arbitrary speculation, and brought within the precincts of science.

In BRODIE'S experiments, a quantity of pure dry oxygen, after having been submitted to electrization by its passage through a modified form of SIEMENS' induction tube, carefully maintained at a low temperature, was collected in an oil of vitriol gasholder, to the amount of 4000 or 5000 cubic centimètres. From the store of ozonized gas thus collected, which was found to maintain its proportion of ozone without appreciable deterioration for several hours, portion after portion was allowed to pass into a pipette of about 250 c.c. capacity, by displacement of the oil of vitriol originally filling it; and successive equal volumes of the store of ozonized gas so measured off were submitted one after another to the same or different reagents, by the passage of each pipetteful of gas through a small bulb-tube containing the reagent in solution.

The gas, freed from all ozone by its passage through the reagent, was next received into a mercurial measuring cylinder, by which it was expanded to a definite volume, and then by reading off the pressure at which it occupied this volume its proper volume was ascertained.

Finally, the difference between the capacity of the pipette and the volume obtained in the mercurial cylinder showed the volumes of the gas absorbed by the reagent; the weight of this gas being determined directly or indirectly by titrations of the reagent.

Very many points of detail in the construction and use of the apparatus had to be attended to, in order to insure trustworthy results; but both in its

principle and general working the process is exceedingly simple. One essential novelty consisted in the application of the pipette to the purposes of gas analysis; and by its aid results, having an accuracy far greater than those furnished by any previous method of ozone investigation, were found to be obtainable with both speed and facility.

Operating with this apparatus, BRODIE succeeded in establishing three perfectly definite classes of ozone reactions—the first of these including the instances previously made known by ANDREWS and TAIT. In this first class of reactions, of which there are several distinct varieties, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen is unattended by any diminution in the volume of the gas; or a volume of ozone, O^{2+x}, is resolved into an equal volume of free oxygen, and an indefinite weight of oxygen, absorbed by the reagent employed to effect the decomposition.

This class of reactions accordingly does not afford any information as to the value of x, or, in other words, as to the relationship of the formula O^{2+x} to the formula O^2.

Unit Volumes.

$$\overbrace{O^{2+x}}^{} = O^2 + xO \text{ absorbed.}$$

In a second class of reactions, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is attended with a diminution of the volume of the gas equal to half the volume that the weight of oxygen absorbed would occupy in the free state. In this class of reactions, then, one of but two occurrences must happen: either the ozone present in the mixture of gases is absorbed wholly without decomposition, in which case the density of ozone must be twice that of ordinary oxygen, and the formula O^{2+x} become O^4; or the ozone present in the mixture is decomposed into half its volume of oxygen liberated, and into a quantity of oxygen corresponding to its entire volume absorbed; in which case the density of ozone must be one and a half that of ordinary oxygen, and the formula O^{2+x} become O^3.

Unit Volumes.

$$\left.\begin{array}{l} \overbrace{O^{2+x}}^{} = \text{nil} + 4O \\ 2(O^{2+x}) = O^2 + 4O \end{array}\right\} \text{absorbed.}$$

In a third class of reactions the absorption or decomposition of the ozone present in a mixture of ozone and oxygen is attended with a diminution of the gas, equal to two-thirds the volume that the weight of oxygen absorbed would occupy in the free state; or the weight of the gas absorbed is to the weight of an equal volume of oxygen as 3 to 2. But consistently with this class of reactions the density of ozone must necessarily be one and a half time that of ordinary oxygen, and the formula O^{2+x} must become O^3.

Unit volumes.

$$\overbrace{(O^{2+x})}^{} = \text{nil} + 3O.$$

This last and most important class of reactions, by which the formula of ozone as O_3 is put beyond question, was established by a long series of experiments, made chiefly with a neutral or but slightly alkaline solution of sodium hyposulphite (thiosulphate, $Na_2S_2O_3$), and in a few cases with oil of turpentine.

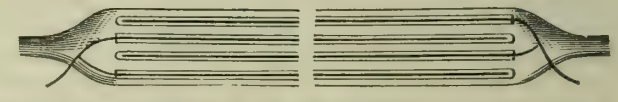
As a result, the ratio of the entire diminution in volume suffered by the original oxygen, to the diminution in volume of the electrized or contracted oxygen effected by the reagent, was found to be, as a mean of twenty-seven concordant experiments made with the hyposulphite, $3.O_2$ to $2.O_2$; and as a mean of eight concordant experiments made with the turpentine, also as $3.O_2$ to $2.O_2$.

But neither with the hyposulphite nor with the turpentine could the weight of oxygen absorbed by the reagent be determined, otherwise than by a calculation from the alteration in volume of the gas. A direct determination, however, was effected in the case of a few experiments made with stannous chloride, under conditions carefully considered and regulated so as to insure a trustworthy result. And it was found in these few experiments, that the weight of the matter of oxygen absorbed from the ozonised gas by the tin salt, was almost exactly three times the weight of the matter of oxygen absorbed from the same gas by potassium iodide—the volume of the weight of oxygen absorbed by the tin salt being almost exactly twice the volume proper to the weight of oxygen absorbed by the potassium iodide. (ODLING, "R. Inst. Proc.").

Ozone may be obtained by the action of the electrical spark, or the glow or silent discharge, on pure oxygen. With the silent discharge a much larger proportion of the oxygen is converted into ozone than with the spark; and if sparks are passed through oxygen containing its maximum amount of ozone, the greater part of the ozone will be rapidly destroyed, or rather changed back into ordinary oxygen.

The best ozonizers are those on the principle devised by SIEMENS. in which a large surface of gas is exposed to the silent discharge. Fig. 1 is an ozonizing arrangement to be used with an induction coil; eight or ten pairs of tubes made of very thin glass are connected with the terminals in the manner shown. The whole are surrounded by a long glass cylinder, through which oxygen or air is slowly passed. The amount of ozone is increased if the outer tube be surrounded with water.

Fig. 1.



As regards the actual amount of oxygen which, under the most favourable conditions, can be converted into ozone, in an experiment by ANDREWS and TAIT a contraction of one-twelfth of the original volume of the oxygen, or 8·3 per cent., occurred. The largest contraction attained in the experiments of VON BABO and CLAUS amounted to 5·74, and in those of BRODIE to 6·52 per cent. But with the aid

of the excellent induction tube of SIEMENS contractions to the extent of 10 per cent. and more can be attained.

ANDREWS has devised the following apparatus, by means of which the contraction of oxygen in changing into ozone can be shown as a class experiment. The induction tube of SIEMENS, in which the electrical discharge from an induction coil acts upon air or oxygen as it flows between two thin plates of glass, whose surfaces are at a few millimètres distance from each other, is modified as shown in Fig. 2. At *c* it terminates in a capillary tube, the end of which is hermetically sealed, after a stream of pure dry oxygen has been passed through the apparatus for a sufficient time to displace the air. In exact experiments the end, *b*, is also sealed, and afterwards opened under sulphuric acid. For class purposes it will be found sufficient to immerse it quickly under the acid contained in the beaker, *a*, as shown in Fig. 3, where the induction tube is seen surrounded to within 12 m.m. of its upper surface, with water contained in an *insulated* cylindrical vessel, A A'. The internal cavity of the induction tube is also filled with water to about the same level. By means of wires covered with caoutchouc, except at the lower ends, P P', the discharge from an induction coil can

Fig. 2.

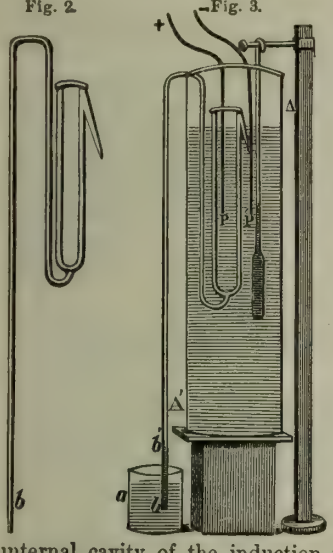


Fig. 3.

be passed through the apparatus. The water in A A is kept as steadily as possible at the temperature of the apartment. Any slight changes of temperature, or of barometric pressure, are noted. In very exact experiments the surfaces of the induction tube should be covered with tinfoil, and the cylindrical vessel filled with ice. Before commencing the observation, the level of the acid should be brought to about *b'*. On passing the electrical discharge the acid will at first be depressed for a few m.m. from the repulsive action of the particles of the electrified gas, but will afterwards steadily rise, and for some time with such rapidity that the ascent of the column can be easily followed by the eye. When the current is interrupted a sudden rise of the acid column will occur, equal to the depression which took place on first making connection with the coil, after which the new level may be read off.

ANDREWS' apparatus for obtaining ozone by electrolysis is shown in Fig. 4. The most convenient liquid for the purpose is a mixture of 1 pint of sulphuric acid and 6 or 8 pints of water; and the lower the temperature at which the electrolyte is maintained during the process, the greater is the amount of ozone. The glass bell jar, *a*, is open below, and contracted to a neck above, into which a bent connecting tube is fused. This bell jar is suspended in a round cell, *b b'*, of porous earthenware, leaving a clear space of 2 inches between its lower edge and the bottom of the porous cell. The whole is placed in a glass jar, *c c'*, of somewhat larger dimensions than the cell; a bundle of platinum wires, *p*, suspended below the bell jar, acts as the positive pole, and a broad ribbon of platinum, *n n'*, placed between the outer glass jar and the porous cell, as the negative pole of a battery of three or four couples.

From the bell jar the mixture of ozone and oxygen disengaged at the positive pole passes to a sulphuric drying tube, *d*, and thence through the connecting tube, *e*, to other tubes for illustrating the properties of ozone. Thus, in the figure, it is represented as traversing a tube of hard glass, *f f'*, covereed with fine wire gauze, and terminating near the surface of the mercury contained in the flask, *h*. So long as the gas is heated strongly by the spirit lamps, *g g'*, as it

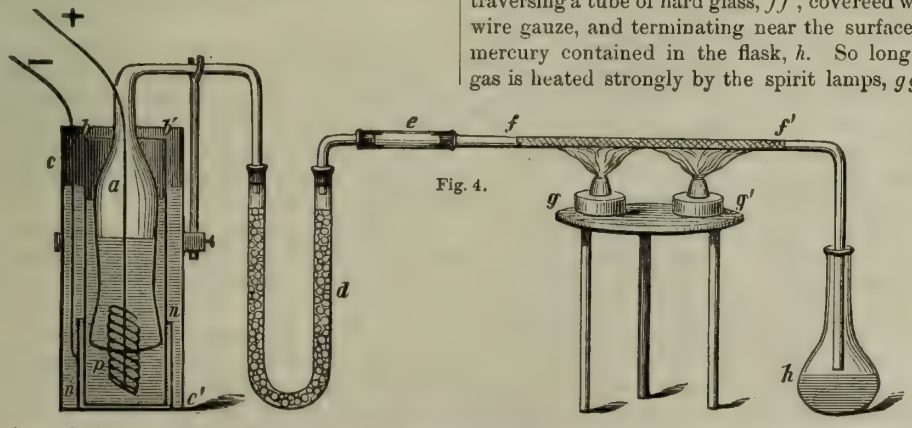


Fig. 4.

passes through the tube, *f f'*, not the slightest change is produced upon the mercury; but when the lamps are removed, and the tube allowed to cool, the mercury is rapidly attacked.

Ozone is also obtained by the slow oxidation of phosphorus, and of certain ethers and essential oils in presence of moisture.

Properties.—Ozone can be preserved, if dry, in sealed tubes at the common temperature of the atmosphere for a very long time; but by slow de-

grees it eventually becomes changed back again into common oxygen. This conversion goes on more rapidly as the temperature is raised, and at 237° C. it is almost instantaneous. One gram. of ozone in passing to the state of ordinary oxygen evolves 355·5 units of heat. (P. J. HOLLMAN).

A similar effect to that of heat is produced by several oxides, notably oxide of silver and binoxide of manganese, which by mere contact, or, as it is termed, catalytically, instantly change ozone into ordinary oxygen. Ozone is also destroyed by agitation with water, provided the ozone is in a highly diluted state. ANDREWS found that dry ozone, even if present in such quantities as freely to redden iodide of potassium paper, is readily destroyed by agitating it strongly with glass in fine fragments, although it may be kept for an indefinite time in sealed glass tubes. This experiment forms a new and closer link than any hitherto observed between a purely mechanical action and a chemical change.

Ozone is a powerful oxidising agent; it attacks metallic mercury and silver with the greatest energy, and converts them into oxides. Its action upon mercury is very striking; a few bubbles of oxygen, containing not more than $\frac{1}{5000}$th part of ozone, will alter wholly the physical characters of several pounds of mercury, taking away the lustre and convexity of the metallic surface, and causing the mercury to form an adhering mirror to the surface of the glass vessel in which it is contained.

If ozone in a diluted state is slowly passed through a tube filled with silver leaf, the metal will be oxidised to the distance of 2 or 3 millimètres; but the oxidations will not proceed further, although the ozone reactions are wholly destroyed. This striking result is due to the catalytic action of the portions of oxide which are at first formed. So small is the amount of oxide produced in this case, that in a glass tube through which many litres of electrolytic ozone had been passed, the increase in weight from the formation of oxide was scarcely an appreciable fraction of a milligramme.

The action of water on ozone, when the latter is present in small quantity, is probably also of a catalytic character. If a bottle containing a little water, and filled with air or oxygen, mixed with a sufficient amount of ozone to redden instantly iodide of potassium paper, is shaken violently for a few moments, all the ozone reactions disappear.

Ozone was supposed to be insoluble in water, but CARIUS has shown that a small quantity is dissolved. He states that 1000 c.c. of distilled water at 0° C. and 0·76 m.m. pressure absorb from 3·86 to 5·41 c.c.

E. SCHÖNE believes that the presence of nitrogen is the reason that so many chemists have obtained negative results in their experiments on the absorption of ozone by water, this gas being oxidised by ozone to nitric acid. By taking the greatest care to avoid the presence of nitrogen and organic matter, he obtained the following results:—1. Ozone does not oxidise water. 2. Ozone is absorbed by water in considerable quantity, even at the ordinary temperature. The observed maximum was 8·81 c.c. (reduced) ozone (O_3) per litre. If the hands are placed in water saturated with ozone, they retain the peculiar smell for some time. 3. In the passage of ozone through water far more ozone disappears than is absorbed, and as the loss continues even after the water is saturated, it would seem that water has in this case the power of breaking up ozone.

Nitro-glycerin, dynamite, iodide of nitrogen, and chloride of nitrogen, all decompose with explosion if placed in a vessel containing ozone (JONGLET). Ordinary gunpowder, under the same conditions, undergoes considerable alteration in the course of a few weeks.

Ozone decomposes a solution of iodide of potassium, liberating the iodine, which may be discovered by its red colour, or its blue compound with starch. If the action is continued sufficiently long the free iodine is oxidised, potassium iodate formed, and the solution becomes colourless.

Reddened litmus paper moistened with a solution of iodide of potassium is turned blue when exposed to the action of ozone, in consequence of the caustic alkali formed by the decomposition of the salt. In employing this test it will be found advantageous to remove the free iodine, by washing the paper with strong alcohol. This form of the potassium iodide test was proposed by HOUZEAU for the discovery of ozone in the atmosphere.

Paper moistened with manganous sulphate becomes brown from the formation of hydrated dioxide of manganese.

Solutions of thallous oxide are in like manner converted into brown thallic oxide, black sulphides of lead into white sulphate, and the yellow ferrocyanide of potassium into the red salt; tincture of guiacum is turned blue.

The bleaching properties of ozone are highly characteristic, and have attracted a great deal of attention. It deprives indigo of its blue colour, converting it into isatin, and readily bleaches litmus and other vegetable colouring matter. In comparison with potassium permanganate its bleaching power is as 3 to 1.

Attempts have been made to apply this property of ozone in the arts, and particularly to the refining of sugar and bleaching of linen. For the preparation of ozone on a large scale from ordinary air, a modification of SIEMENS' tube generator has been devised by BEANES, and is an efficient and powerful instrument.

WIDEMANN invented a process for removing fusel oil from whiskey, and acidifying it by ozone, which was successfully carried out in the United States (see ACETIC ACID).

A. W. WRIGHT repeated these experiments in the following way:—1. By passing alcohol vapour and ozone through a flask heated to 100° C., and collecting the products in a cooled flask. 2. By passing alcohol vapour and ozone through a porcelain tube heated to 200° to 250° C. 3. By passing ozone through a small quantity of cold alcohol in a flask, which was shaken vigorously for ten or twelve hours. 4. By passing ozone through boiling alcohol, and

condensing the vapour in a cold flask. 5. By passing ozone through boiling alcohol in a flask provided with a vertical condenser, so that the condensed liquid was continually subjected to the action of the gas.

In all these experiments the strength of the alcohol used was 91·5 per cent. The alcohol was in all cases oxidised to acetic acid, aldehyde, and hydrogen dioxide. The operation in each case being continued for an hour, the percentage of acid formed relatively to commercial acetic acid, that is, the strength of the dilute acid, was found to be as follows:—

	Per Cent.		Per Cent.
In experiment 1, ...	1·62	In experiment 4, ...	1·18
" 2, ...	0·81	" 5, ...	1·22
" 3, ...	0·32		

Ether when oxidised by ozone gave acetic and formic acids, aldehyde, and hydrogen dioxide.

The sulphur of vulcanized caoutchouc is attacked by ozone. A. W. WRIGHT passed ozonized air through a vulcanized rubber tube, and then allowed it to bubble through water. In a short time the water acquired the odour of sulphurous oxide, and ultimately gave a white precipitate with barium chloride.

The process recommended by P. THÉNARD for determining the quantity of ozone present in a volume of oxygen depends upon the oxidising action which ozone exerts upon arsenious acid, the ozone itself being meantime reduced. The method of procedure is this:—Into a measured flask containing the ozonised oxygen, 10, 12, 15 c.c., according to circumstances, of standard solution of arsenious acid in hydrochloric acid are introduced. The solution is made on GAY LUSSAC'S method, and is of such a strength that it requires about 0·1 milligram. of oxygen to convert the arsenious into arsenic acid. After brisk agitation at short intervals, 30 c.c. of sulphuric acid solution are added, and the quantity of arsenious acid unconverted by the ozone is determined by means of standard solution of potassium permanganate.

Soon after the discovery of ozone, SCHÖNBEIN, having observed that the air of the country frequently coloured a delicate ozone test paper in the same manner as ozone itself, inferred that ozone is a normal constituent of our atmosphere. He concluded that the amount of this body present in the air is different in different localities, and in the same locality at different times, and with great boldness he attempted to connect its presence with the prevalence or rarity of certain catarrhal affections.

To determine the actual amount of ozone in the atmosphere is a problem of surpassing difficulty, on account of the extremely small proportion in which it exists, even when at a maximum. Its presence can be easily discovered by any of the ordinary iodized starch papers, or even more readily by white bibulous paper which has been moistened with a dilute solution of iodide of potassium, and allowed to dry spontaneously in a dark room. If a slip of this paper is exposed for five minutes to a current of air, which will often be supplied by the wind, or may be produced by walking briskly, it will be found to have acquired a delicate red tint if ozone be present even in the smallest quantities. The tint will be best observed by comparing the slip after exposure with another slip of the same paper which has not been exposed. The action of the diffused light of day on the paper is rarely perceptible after so short an exposure; but this source of error can be easily avoided by inclosing the paper in a hollow cylinder of wood.

Although, with the experimental resources now at our command, we can scarcely venture even to estimate the actual amount of ozone at any time present in the atmosphere, yet it may be possible, as SCHÖNBEIN long ago proposed, by applying a chromatic scale to the indications of the test-papers, to ascertain approximately its relative amount in different localities, and its variations in the same locality. Such estimates must, however, be most uncertain, since the shades of colour produced on test-papers hardly admit of being defined by numbers; and in this particular case they are liable to a special source of error, as there can be little doubt that a large but unknown part of the ozone in the air which comes in contact with the paper is catalytically destroyed, and produces no chemical effect whatever. At the same time the ozonometer, especially when used with an aspirator, does unquestionably give indications of value regarding the ozone states of the atmosphere; and, till more accurate methods are devised, these observations ought certainly to be continued.

Ozone is rarely found in the air of large towns, unless in a suburb when the wind is blowing from the country; and it is only under the rarest and most exceptional conditions that it is found in the air of the largest and best ventilated apartments. It is, in fact, rapidly destroyed by smoke and other impurities which are present in the air where large bodies of men have fixed their habitations. ANDREWS has observed this destructive action at a distance of one or two miles from a manufacturing town, even in fine and bright weather.

Ozone is rarely, if ever, absent in fine weather from the air of the country; and it is more abundant, on the whole, in the air of the mountain than of the plain. It is also said to occur in larger quantity near the sea than in inland districts. It has been found to an unusual amount after thunderstorms—a fact which is favourable to the view that the presence of ozone in the atmosphere is due to the action of the free electricity of the latter on the oxygen of the air. The amount of ozone in the air is greater, according to some observers, in winter than in summer, in spring than in autumn; according to others, it is greater in spring and summer than in autumn and winter.

PAPER.—*Papier*, French and German; *Papyrus*, Latin; παπυρος, Greek, said to be formed from παω, to feed, and πυρ, fire.—This derivation of the Greek name for the plant (papyrus) clearly indicates

the purpose to which it may be supposed to have been formerly applied.

Before the use of papyrus as a material on which records intended for a future generation might be inscribed, men employed stones, either forming them as commemorative structures, or inscribing upon them, when so formed, pictorial hieroglyphics. Stonehenge, in Wiltshire, may be taken as an illustration of the former use; and the monuments of Egypt, supposed to have been erected nearly 2000 years before Christ, are illustrations of the latter. The soft metals, especially lead, were also in use in early times.

Papyrus.—Paper as an article of manufacture is said to have been known to the Chinese about 150 years B.C. At or about the time when they thus made an article on which characters could be inscribed the Egyptians began to employ the papyrus plant. A manuscript of the "Antiquities of Josephus" on papyrus still exists; and it has been proved that paper made from the papyrus plant, 1822 years B.C., was in existence in the eighth century A.D.

The papyrus is a bulrush which grows in the Nile and the marshy swamps connected with that river. Boats as well as paper were made from it. Isaiah alludes to the former (chap. xviii. ver. 2)—"in vessels of bulrushes;" and to the latter (xix. ver. 7)—"the paper reeds by the brooks." It was in one of these papyrus or paper boats, made as described in Exodus (chap. ii. ver. 3), that Moses was "laid in the flags by the river's brink."

Pliny describes the mode of using the papyrus plant for the making of paper as follows:—The papyrus was cut before reaching maturity, being then in a soft and spongy state, and was divided by a peculiar needle into thin plates or pellicles, which were laid lengthways on a table alongside of each other, with their edges touching. Another layer was laid across at right angles. These were moistened with warm water and then pressed, which caused them to adhere, so that the two layers became one compact sheet. After it was pressed, it was dried in the sun, and was then steeped in a size or starch, made by pouring boiling water on bread and filtering the liquor through a cloth, after which the leaves were again dried in the sun. The finer kinds used for writing are supposed to have been made from the inner part of the stem, while the coarser were made from the outer rind, and were used for packing.

It may be mentioned that, if reliance can be placed upon Chinese records, the very early history of their kingdom was written upon plates of bamboo, which were destroyed in one of their dynastic wars. Books of this primitive nature may be seen among the curiosities in the King's library at the British Museum. As a vegetable substance for writing on, bamboo is more ancient than papyrus. Recent experiments in reference to this plant have led to the expectation that it may be profitably employed for the manufacture of paper in the present day. An account of the proposed method will be given in its proper place.

Parchment.—Jealousy on the part of the Egyptian authorities, lest in other countries a library equal to that at Alexandria should be formed, led to a prohibition of the export of papyrus. This is said to have prompted Eumenes, king of Pergamos, to utilize the skins of animals. Little change has been made in the mode of preparing skins for writing upon; but a very efficient substitute for these prepared parchment skins was proposed by Mr. Gaine. The manufacture of this parchment paper, or vegetable parchment, as it is sometimes called, has become so important, that an account of the plan adopted is given below.

The skin of any animal might, with proper treatment, be converted into a suitable material for writing upon; but, according to Dr. Ure, the following list gives the only skins extensively employed, and the uses to which they are put.

Skin of.	Employed for.
Sheep or she-goat,	Parchment.
Calves, kids, and dead-born lambs,	Vellum.
He-goat, she-goat, and wolves,	Drum-heads.
Ass,	Battledores.

Vegetable Parchment.—In 1857 Mr. W. E. Gaine took out a patent for a very interesting and important process, whereby ordinary unsized paper, such as blotting or filtering paper, can be at once converted into a tough transparent substance, almost impervious to moisture, and possessing several valuable and remarkable properties. The process consists in immersing the paper in a mixture of 2 parts of oil of vitriol and 1 part of water at the ordinary temperature for a few minutes; and it is found that if the mixture is not formed exactly in this proportion, or even if one portion of the paper treated be less moist than another portion, the experiment is unsuccessful. Great care is also required in removing every trace of acid from the fibre; and with this object it may, after being carefully washed, be treated with a very dilute solution of ammonia, the final traces of sulphate of ammonia being removed by further washing, and traces of ammonia by lime or baryta, after which it is simply dried.

Leaves.—The leaves of some kinds of plants, after undergoing a process of drying and rubbing, make a tolerable writing material; and Mr. Herring says that the natives of India use them in preference to paper for ordinary correspondence.

Although the substances previously enumerated have been all used for writing upon, they would, however suitable for that purpose, have been altogether useless for printing. The papyrus was too hard and brittle either to receive an impression, or to resist heavy pressure. The mode of writing upon it, with a style or sharp metallic point, shows that it was not suitable for printing. It is therefore by no means wonderful that the art of printing was not discovered in the earlier ages of the world.

Paper.—Very little information can now be obtained of the invention and early progress of the art of paper-making. The earliest accounts do not agree either in regard to date or place; but there is little doubt that the principle of the modern art of reducing vegetable fibre to a liquid state is of Chinese

origin, dating from about the beginning of the Christian era. The first accounts of paper bearing any resemblance to the article now manufactured date from the tenth century. Gibbon says that the knowledge of the inestimable art of making paper from linen rags was diffused from the manufactures of Samarcand over the western world; and he adds, that the librarian Cassire relates from credible testimony that paper was first invented, or rather introduced, at Mecca by Joseph Amru, in the year 706 or 710.

The art reappears in Germany during the fourteenth century; but as early as 1290 a paper-mill is said to have existed at Ravensburg. A mill was erected at Nuremberg in Germany, to make paper from linen rags, by Ullman Stromer, in 1390. At this time the process was kept strictly secret, and the workmen were sworn not to divulge it or carry it on on their own account. Notwithstanding all these precautions to keep the art secret, it became known, and was introduced into France, Holland, and Genoa, in all of which it seems to have been prosecuted with success, particularly in France, whence there was a considerable quantity exported to England and other countries. The trade began to decline in France about the middle of last century, as other countries, particularly Great Britain, were by that time manufacturing nearly sufficient for their own use.

The first paper-mill in England, of which there is any particular account, was erected at Dartford in Kent in 1588, by Sir John Spielman, a German jeweller in the employment of Queen Elizabeth. Herring says it is quite certain that paper-mills were in existence long before Spielman's time, and adduces a passage in Shakspeare's play of "Henry the Sixth," in which reference is made to a paper-mill at least a century before this; and while he admits that the chronological accuracy of Shakspeare is not to be depended on, he points out that the earliest traces of the manufacture in this country occur in a book published by Caxton in 1490. The mill to which reference is supposed to be made was near Stevenage in Hertfordshire. In the household book of Henry VII. there is an entry of a reward of 16*s.* 8*d.* given to the *paper mylne*, dated 25th May, 1498; and again in 1499 another reward of 6*s.* 8*d.* is given to *Tate of the Mylne*, supposed to be the mill at Stevenage.

About 1685 white paper, of which little had been made, began to be more generally manufactured, and the quantity rapidly increased. It was estimated that about 300,000 reams were produced in 1721, and this was supposed to be about two-thirds of the consumption of the country.

Manufacture of Paper.—*Materials.*—Formerly vegetable substances, and more especially linen and cotton rags, which could be obtained with comparatively little difficulty, were exclusively employed for the manufacture of paper; but as the demand for it increased, great fears were entertained that the supply would fall short, the sources from which it was drawn not being thought to be of so elastic a nature as the enormous consumption of paper rendered necessary.

The difficulties in finding a thoroughly efficient substitute were very great, and even at the present day no material has been found which satisfies all requirements. The principal advantage possessed by rags is peculiar, and consists in the circumstance that in their conversion from raw vegetable fibre into woven fabrics they have undergone a thorough cleansing, and have been subjected to certain operations, all of which tend to make them suitable for the manufacture of paper, and through which the raw material, if used directly for the manufacture of paper, would in a modified form have to pass. As, therefore, the cost of such treatment has already been met in the purchase of the new material, whether it be linen, calico, or any other manufactured fibre, the paper manufacturer is relieved from this expense and labour, and the cost of finished paper can be lowered in like proportion. Moreover, no other manufacturer competes for the purchase of worn out linen or cotton goods, they being neither ground up to make shoddy, as are some descriptions of old woollen goods, nor used either for manure or tinder. It is a remarkable fact, and abundantly proved by statistics, that although the quantity of paper produced per annum increased nearly fourfold between 1830 and 1860, the price of rags remained nearly constant, and was, in fact, slightly lower in the latter year: in 1830 they varied, according to quality, from £45 to £10 per ton, and in 1860 from £38 to £10. The tax on paper was, however, repealed in 1859, and its influence was very perceptible in 1861, since which date the produce of paper has increased very much, and the price of rags, &c., has become so excessive as to render it imperative that some efficient substitute should be found.

The following list of the principal materials which have been proposed from time to time for employment in the manufacture of pulp, is taken chiefly from an article by Professor Archer in the excellent series of manuals on British Manufacturing Industries, recently issued. Those in italics are now more or less in use in this or other countries.

Linen rags, flax, *flax tow*, and refuse.

Cotton rags and cotton wool.

Old ropes (junk), *oakum*, *hempen canvas*, and sacking.

Old sacking and gunny cloth, made of jute.

Alfa or *Esparto grass*, *wood of various kinds*, *straw*, *maize husks*.

The dwarf palm (*Chamærops humilis*).

Leaves of American aloes (*Agave*).

Leaf-stalks of the banana, plantain, and the *manila* or textile banana (*Musa textilis*).

Bamboo and rattan canes.

Stems of the horse bean, French bean, and scarlet runner.

Hopbines, nettles, thistles, mallow stems.

New Zealand flax, sugar-cane refuse, tobacco and potato stalks.

Beet-root refuse from the sugar-works.

Grasses, clover, lupin stalks, sunflower stalks.
Various rushes, the yellow iris, bryony roots.
Twigs of the common broom and heather.
Rhubarb stalks, mustard stems (after thrashing).
Pine-apple leaves and the sea-grass (*Zostera marina*).
The bark of the baobab tree (*Adansonia digitata*).
Gombo.
Zizania straw.
Miscellaneous substances, vegetable and animal:—
Peat, moss, and bracken fern.
Sawdust, spent tan, bast matting.
Barks of various trees, especially the *paper mulberry*.
Floss silk, wool, fur, leather waste.
Asbestos, cotton-seed husks.

Before proceeding to give an account of the several manufacturing processes, it will be well to describe briefly the more important substances contained in the above list.

According to SCHÜTZENBERGER, the pulps derived from the various materials other than rags range themselves, as regards quality, in the following order:—

(1) Pulp formed from Esparto grass.
(2) " " Wood.
(3) " " Rye.
(4) " " Wheat straw.
(5) " " Oat straw.
(6) " " Barley straw.
(7) " " Buck wheat straw.

Rags.—The system adopted in the sorting of rags will be presently explained, and it will be sufficient here to mention a few general facts with reference to them. Their quality varies much with the locality in which they are collected. Thus those from great centres of population are fine and white, and the steps taken to bleach the materials have reduced the strength of the fibre. Country rags, on the contrary, are coarse, strong, and of a greyish colour, and frequently contain pieces of newer material added for repairs.

Care should always be taken that the rags, if stored, are dry, as otherwise they are liable to take fire owing to the heat generated by fermentation; and even if this were not the case it would be very detrimental to the toughness of the fibre. Old rags are almost pure cellulose, that is, their composition is as follows:—

Carbon,	44·44
Hydrogen,	6·18
Oxygen,	49·38
	100·00

From which the formula will be seen to be $C_{18}H_{30}O_{15}$.

Esparto Grass.—Of the various materials from time to time suggested for the purposes of the paper manufacturer, in addition to or as a substitute for rags, none have attained to the importance of "Esparto," or "Spanish grass." In 1856, when first introduced, about 40 tons were imported, and now the consumption has risen to nearly 150,000 tons per annum. The first price was £4 per ton; it is now £10 per ton, and there is every reason to expect a still higher price. This rapidly extended demand for an article which was deemed of little or no value in Spain, and which was considered as cumbering the soil, soon began to tell upon the quantity that could be brought into the market, and a considerable amount of attention was directed to the cultivation of Esparto. Then it became obvious that no ordinary care could keep production in advance of demand, for the young seedling was not only delicate, but its growth for the first two years was scarcely perceptible. Indeed, before the plant develops serviceable fibre a period of ten or twelve years must elapse. If then duly cared for it may live to a great age.

The Esparto is indigenous to Spain, where it grows wild in almost all parts, and resembles very much the common spear grass which is found on the sandy shores of Lancashire. It has long been used in Spain for making matting, cords, baskets, &c., and appears to have been employed for such purposes by the Phœnicians, who gathered it in large quantities from the coasts. It grows where few other plants will grow, even on igneous mountains and sterile rocks, and on the sea shore. It is also met with in the northern districts of Africa.

The fibre of the leaf is the part of the plant required. The leaves are carefully separated from the plant between July and October, and it is essential that the harvesting take place in dry weather. In wet weather the stems are not unlikely to be drawn up, and sent in bulk to the paper manufacturer; thus not only giving him what is useless, but destroying a plant which requires so long to develop.

Various attempts have been made to manufacture paper from Esparto during the last forty years. No material alteration for this purpose is needed in the machinery generally used; indeed much less power is required. The successful working of the fibre seems to depend mainly on the careful and proper adjustment of the quantity and strength of the chemicals employed. The soda-ash required to neutralize the gummo-resinous matters, and the bleaching powder to bring the product to a suitable colour for printing, are five or six times as much as are needed for bleaching and cleansing the coarsest rags.

The grass is found on analysis to contain in 100 parts—

Water,	9·62
Oil,	1·23
Albuminous matter,	5·46
Starch, gum, sugar,	22·37
Mineral substances,	5·04
Fibre,	56·28

Wood yields two products of great importance in the manufacture of paper. They are (1) the so-called mechanical wood tissue, obtained by grinding wood; and (2) the cellular tissue, or wood-cellulose, obtained by the action of chemical agents on the wood. The latter of these yields a substance of striking compactness, and can be used for making the best qualities of paper.

In 1865 a large factory for the preparation of wood by chemical means was established near Philadelphia; but owing to want of machinery, &c., it was found impossible to prepare the pulp at a remunerative cost. Since that time, however, several mills have been profitably worked; and in 1871 an English and Swedish Company set up five large factories in Sweden. Germany possesses about six such factories. Recently mills have been erected for preparing pulp from wood in Norway and Sweden, thus avoiding the cost of transport to the chief paper-producing countries of a large quantity of useless material. The timber is converted into pulp, either by the grinding process invented by Voelter, or by boiling with chemicals, and the half-stuff is dried and compressed into cakes for exportation. It is, however, not used extensively in this country; and Belgium is one of the chief producers of paper from wood.

Straw.—Although straw unmixed with rags can be used for the manufacture of writing paper, it is of very inferior quality, entirely lacking in the strength which rags impart. A useful brown paper can, however, be prepared from it, and it is extensively used in conjunction with rags.

The straw most suitable for conversion into paper is that obtained from wheat; but oats, rye, and barley may be used. The principal difficulty in the preparation consists in the removal of the silica present; hence wheat straw, which contains the smallest quantity of this substance, is the most easily treated. Considerable care is required in the purchase of straw by the manufacturer, as the value is materially diminished if it has been exposed to the weather, after being cut, for some time, as this causes rotting to ensue. Care should also be taken to avoid such as has been carelessly harvested, so as to include impurities, such as grain, weeds, chaff, &c. It may be mentioned that only oats, wheat, rye, and in some districts barley, can be obtained in such quantities as to be of service in the manufacture.

The following table gives the results of a number of experiments made by C. Schmidt, in order to ascertain the relative values of various materials to the paper maker; and it shows in a striking manner that foliage contains but a small quantity of fibrous matter, and is therefore of no service; whereas wheat and bean straw, and in a still greater degree rapeseed straw, are eminently suited for conversion into pulp.

	Foliage of Oak Trees.	Poplar Foliage.	Bean Straw	Pea Straw.	Barley Straw.	Oat Straw.	Lens Straw.	Corn Husks, Maize Straw.	Rape-Seed Straw.	Rye Straw.	Wheat Straw.
Parts extracted by water,	25·00	28·00	10·67	46·60	11·33	20·67	27·47	17·00	14·80	2·80	7·60
Parts extracted by a weak lye of potash,	57·00	48·36	37·42	23·24	38·24	31·62	34·16	57·03	29·80	49·08	40·43
Wax, resin, and chlorophyll,	3·00	2·88	0·91	1·54	0·78	0·77	1·27	1·74	0·50	0·52	0·47
Fibre,	15·00	20·76	51·00	28·62	49·65	46·94	37·10	24·23	54·90	47·62	51·50

Supply of Materials.—To investigate the causes which have influenced the demand for the raw material for the making of paper during the last twenty years is not the province of this article. It may, however, be assumed that certain causes have materially stimulated every industry in which paper is involved; hence the necessity for a largely increased and increasing supply. Hitherto vegetable fibre has been considered as *the* source whence to look for this increase. These fibres are so various that inquirers in any one district are apt to appreciate too highly the fibre of most ready access.

This may account for the sending to the English market of many fibres which, whilst hopeful, are yet of much less value than those from other districts, and which can be imported at a less price. To the International Exhibition in London in 1872, India sent two cases containing specimens of thirty-three fibres from that country. There were also samples of paper made from twenty-eight various materials—all products of the vegetable kingdom.

The geographical area from which rags—the original raw material of paper—are now collected is of very remarkable extent. They are brought to Great Britain from almost every country; they come hither even from Japan and the most remote states of South America, as well as from the continent of Europe. The bags containing them are generally transmitted in the condition in which they have been imported to those who purchase them for paper-making. The rags collected in England for the most part pass through the hands of wholesale merchants, who are chiefly to be found in London, Liverpool, Manchester, and Bristol, and are more or less sorted before being sent to the manufacturer. The trade, however, do no more than this rough sorting; no process is adopted by the merchants for either cleansing or disinfecting the goods. The sorting necessarily discovers certain rags that are useless for the paper manufacturer. These are used as manure, particularly where hops are grown. The woollen rags are not generally mixed with the cotton ones, although when in the cloth manufacture flax and wool have been combined, there is a process by which such rags may be converted into paper; yet as a general rule the woollen materials (of which some millions of pounds are annually imported) are formed into "shoddy."

Waste paper, old ledgers, railway tickets, and even the minute disks punched from postage stamp sheets, are sent with rags as valuable material for the paper manufacturer. Indeed, the wish to utilize waste material in one branch does at times affect the industry in a distinct branch. Formerly all the refuse blowings and droppings from silk and cotton mills were available for the paper maker; now these have a high textile value, and form the basis of a distinct trade, as in the manufacture of wadding, common carpets, twine, &c.

Preparation of Rags.—We shall endeavour, in

the following account, to make some mention of all the more important processes now in use.

Thrashing.—The large quantities of dust and miscellaneous refuse unsuited to the purpose for which the rags are to be employed, which are naturally present from the circumstances of the case, and are not unfrequently added in the form of sand, &c., to increase the weight, render it necessary that they should always undergo a preliminary dusting; and this is the more desirable on account of the health of the work-people, and of the preservation of the machinery through which the rags subsequently pass. This operation is usually performed in a rotating wire drum, provided with beaters inside. In addition to the loss in weight, owing to the removal of impurities during this operation, a small loss of the fibre also occurs.

The *duster* subsequently described may be used for this preliminary operation, but a specially constructed appliance called a *thrasher* is preferred. One form of this apparatus consists of a wooden box, divided horizontally by a semi-cylindrical division of gauze or perforated iron; in the upper portion the box is provided with strong teeth, and a wooden horizontal drum armed with similar teeth is caused to revolve, so that the fixed and moving teeth pass alternately between each other; the rags, being introduced through doors into this space, are effectively purified, the dust passing into the portion of the box below the gauze division.

Sorting.—Several circumstances must be taken into account in preparing the rags before they are passed on to the processes necessary for the manufacture of paper. These depend on the nature of the fibre composing the rags; that is, whether they consist of linen, silk, cotton, hemp, or wool, the thickness of the substance, the state of wear, and finally the colour. Blue rags are usually separated from the rest, and are employed for the manufacture of blue paper, whereas most of the others require bleaching. The finer qualities are set aside for writing paper, and the inferior qualities may be used separately, or mixed in various proportions according to the experience of the manufacturer; and considerable skill is required in order to avoid, on the one hand, waste of the better qualities, and on the other, an inferior colour and quality in the paper produced. The canvas sacks in which the rags are brought to the mill are worked up into the coarser qualities of paper.

British paper makers usually classify the rags collected at home under the following fourteen heads:—

New Cuttings, Fines (whites), Outshots (whites), Seconds (whites), Thirds (whites), Colours or Prints, Blues, Gunny Clean, Gunny dirty, Rope (hard), Rope (white), Rope Bag, Bagging, Hand-Stuff.

And the foreign rags are thus denominated:—

Hamburg.

S.P.FF.	C.S.P.FF.	C.F.B.
S.P.F.	S.F.X.	C.F.X.
FF.	L.F.B.	F.R.
	L.F.X.	

Trieste.

S.F.	F.	B.M.	M.O.
O.	C.B.	C.C.	C.T.

Leghorn.

Linens, P.L.	Cottons, P.C.	S.C.	T.C.

Alexandria.

Cottons, White.	Cottons, Blue.	Coloured.

The sorting is usually performed by women, whose duty it is, not only to classify the various qualities, but to remove all materials, such as buttons, hems, knots, hooks and eyes, india rubber, &c., which would either be detrimental to the paper produced, or liable to injure the machinery.

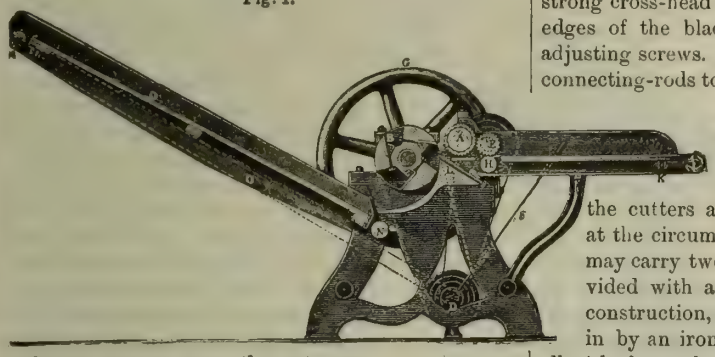
The rags are again examined by women called *overhaulers*, or *overlookers*. There is generally one overhauler to every eight or ten cutters. Some manufacturers attach great importance to having their rags cut into pieces 4 inches square. But the mere size of the rags is a matter of indifference. The principal object is to have them in a state which will insure their thorough cleansing in future processes, and cause them to float among water in the rag-engine without twisting and warping round the roller. Anything smaller than is necessary for this purpose causes a greater loss of fibre in the willow and duster.

Cutting.—When this process of dividing the rags into small fragments, with a view to their being converted into pulp, is performed by hand, as is frequently the case, it is usually accomplished, at the same time as the above process of sorting, by women. Each stands in front of an oblong box covered with a coarse wire netting, containing three threads per linear inch, in the centre of which is fixed one or more large-bladed knives, with their backs towards the operator. She is surrounded by a number of small boxes, according to the extent to which the sorting is carried, and these may conveniently be mounted on wheels in order to facilitate their removal. The immense demand for paper rendered it very desirable that this process should, if possible, be accomplished by machinery; but it is a case in which a certain limited amount of intelligence is essential, and although machinery has been introduced for the purpose, it is only employed for the coarser papers, and cutting for writing paper is still performed by hand. Moreover, it is evident that a machine would be unable to always divide raw material in the direction of the fibre, a fact which would occasion some waste in the subsequent treatment.

Rag *cutters* of various forms are in use. Those provided with a self-acting feed are evidently much to be commended, for the accidents arising from the use of hand-fed instruments are very numerous. Fig. 1 represents a cutter provided with a feed roller, A, 4 or 5 inches in diameter, and provided with conical pins over its surface. The revolving knives are of cast iron, and are permanently fixed in the frame, B. They pass in their rotation close to the projecting steel lip, L, and they remain

sufficiently sharp; it is therefore only necessary to advance them from time to time by means of the set screws shown in the figure. Motion is communicated to the shaft, D, and this causes the shaft, E, to rotate, as well as that carrying the cutters and a small roller, M, which gives motion to an apron in

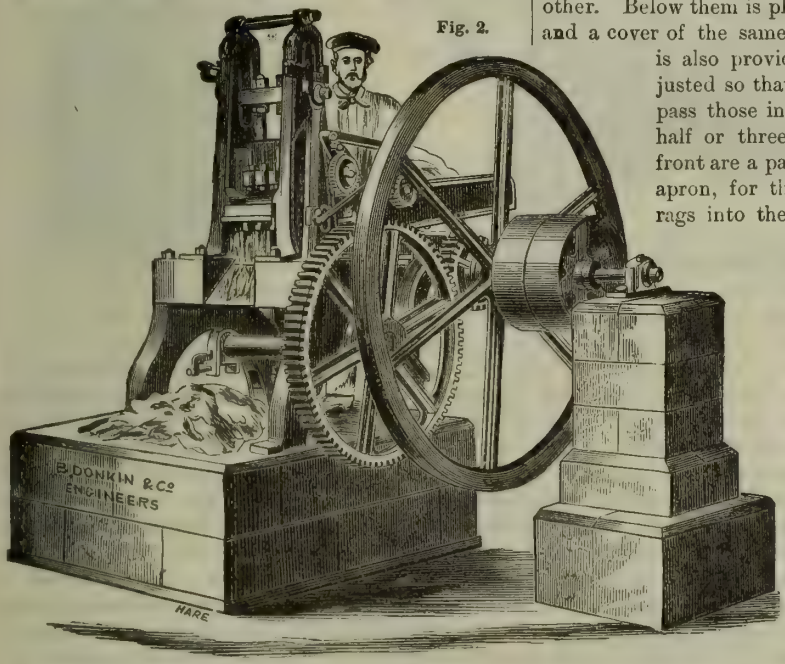
Fig. 1.



order to convey away the cut rags. E and D are provided with cone pulleys, in order to regulate the rate of feed according to the nature of the rags under treatment E communicates its motion both to A and to the apron, H K, by which the rags to be operated upon are introduced.

The rag cutter designed by B. Donkin & Co., shown in Fig. 2, is capable of cutting from 8 to

Fig. 2.



10 cwts. of rags, ropes, hemp, and such like material in an hour. The materials are placed in a feeding trough, and pushed forward by an attendant, until brought under a strong leather endless band provided with leather cross ribs. This band passes over a pair of grooved wooden drums, and under a series of light grooved rollers; and an intermittent motion is given to it by pawls acting on ratchet wheels fixed on the axles of the grooved drums. The cutting is effected by a large knife 9 inches wide, and extending the whole width of the trough, supplemented by three narrower knives at right angles to it. By this arrangement a division of the material in two directions at right angles is simultaneously effected. All four knives are fixed to a strong cross-head working between guides, and the edges of the blades can be set level by means of adjusting screws. The cross-head is coupled by two connecting-rods to a crank-shaft below, which carries a spur-wheel. This wheel is driven by a pinion on the same shaft with the belt pulleys.

In another form of apparatus the cutters are caused to revolve, being fixed at the circumference of a heavy wheel, and this may carry two, three, or four knives. It is provided with a self-acting feed of the ordinary construction, and some makers cover the whole in by an iron hood, a precaution which avoids all risk from the cutters. This form is specially serviceable for treating coarse rags, rope, sail cloth, &c.

Willowing of Rags.—At this stage the rags in some mills are taken to the *willow*, which consists of two cast-iron cylinders, $2\frac{1}{2}$ feet in diameter, and $3\frac{1}{2}$ feet wide, covered with iron teeth projecting about 4 inches. These cylinders are set one behind the other. Below them is placed a semi-circular screen, and a cover of the same shape above. This cover is also provided with teeth, and is adjusted so that the teeth in the cylinders pass those in the cover at a distance of half or three-quarters of an inch. In front are a pair of rollers and a revolving apron, for the purpose of carrying the rags into the cylinders. These revolve with a rapid motion, and the rags, being thrown by the first into the second, are confined in the cylinders about twenty seconds, when a sliding door, which rises three times in one minute, allows them to be discharged into a duster. As often as this sliding door opens the revolving apron moves forward, and charges the willow with a fresh supply of rags. The latter, being thus beaten and teazed in the willow, are loosened in texture, and a large quantity of sand falls through the screen underneath.

Dusting.—As the presence of miscellaneous dust and dirt is very detrimental to the paper, it is necessary that this be perfectly removed while the rags are in a dry state; and even when they have been subjected to the preliminary process of thrashing it is necessary that they pass through the

"duster." This is usually a wire cage or drum inclosed in a box, and caused to rotate; and a number of arms in the interior rotate, generally in the reverse direction to the drum itself. The drum being placed on an incline, the rags, which are introduced at the upper extremity, pass through it, and escape at the lower end.

The "devil" is a more powerful appliance, and is specially useful, therefore, for the treatment of coarse and very dirty rags, hemp, oakum rope, &c. The principle on which it acts is similar to that of the thrasher; but the revolving axle is conical, and carries a series of teeth arranged on it in a spiral form. The case, also, in which it rotates is circular instead of being square, and the rags are fed continuously instead of intermittently. It usually makes about 300 revolutions per minute, while the thrasher only rotates at about one-tenth of this velocity. The use of this apparatus facilitates the subsequent operations; but it, of course, requires more power than ordinary dusters, and is said to cause considerable waste.

Boiling.—The principal object of this operation is to remove any grease the rags may contain, by means of a caustic alkali; and the process considerably aids the subsequent bleaching in that it weakens the adherence of any colouring matters to the fibres.

Rags are boiled also for the purpose of *killing* minute particles of the stem of the flax and shell of the cotton, which even very fine cloth contains. These substances, which are generally called *shove*, are very injurious to paper, and boiling is the only way to get rid of them. It also loosens the dirt in the texture of the rags, and considerably improves their colour. A strong flax rag will lose from one-third to one-fifth of its weight by boiling and washing.

The boiling was formerly conducted in a plain cast-iron vessel which was capable of containing about 1 cwt. of rags. Various modifications were introduced into this crude apparatus, and now either cylindrical or spherical rotating boilers are universally employed, the heat being obtained by injecting steam, which may or may not be superheated. The alkali employed is usually either quenched lime or caustic soda. A caustic alkali prepared by boiling lime and carbonate of soda together is also frequently employed. While seething it should be well stirred and mixed, and afterwards allowed to stand for a few hours, until the sediment falls to the bottom, when a clear liquid is obtained. The quicklime is first thrown among the hot water, and some think it improves the lye to introduce the soda immediately, while the lime is slaking, as a high degree of heat is then evolved, which dissolves the soda very quickly. Others slake the lime in a cistern by itself, and, after stirring well, allow the heavier and undissolved portion to fall to the bottom, then run off the upper portion, which has the appearance of a fine thick cream, into another vessel, and afterwards put in the soda. Another method is to dissolve the lime as above, and run it into the boiler among the rags; the quantity of soda to be used is then put into a bag, which is introduced into the boiler and its contents allowed to dissolve. But the general way is to mix the lime and soda, and run the clear liquid into the boiler. For the finest papers this liquid should be quite pure: 6 to 10 lbs. of soda, and 3 to 5 of lime, are generally used for 1 cwt. of rags; but this proportion varies according to the quality of the rags, and every manufacturer has his own method of procedure.

Fig. 3.

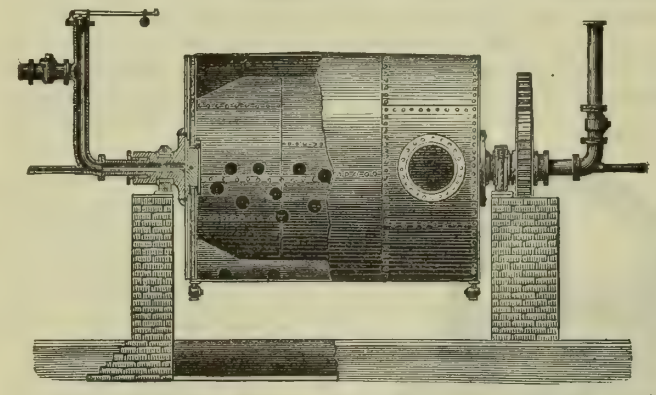
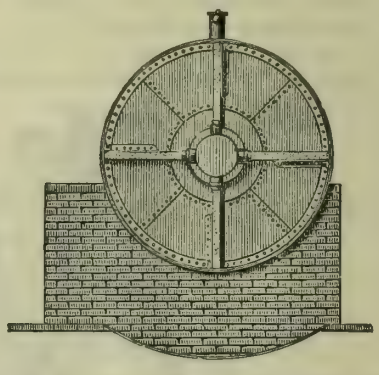


Fig. 4.



As an example of boiler working at the atmospheric pressure we may mention the apparatus devised by Coupier in 1858. It consists of four cylindrical boilers provided with false bottoms, on which are placed the rags saturated with lye. The cylinders are closed by lids from which rise tubes provided with taps. Steam is introduced below the false bottom of each boiler. The four boilers are so connected that the tube from the top of each enters one next to it in the space between the two bottoms, and any connection can be closed at will by the above-mentioned taps, an arrangement which renders it possible to perform the different stages of the operation in the four boilers simultaneously. Thus, calling them 1, 2, 3, and 4, the operations taking place at any given time will be as follows:—

In No. 1 steam is entering between the bottoms, and the boiling process is taking place.

In No. 2 the condensed steam from No. 1 enters, and gradually passes up through the mass which has just been boiled, and washes it.

In No. 3 the mass is being withdrawn from the boiler.

In No. 4 a fresh charge is being introduced.

When the boiling in 1 has been sufficiently prolonged the tap between 1 and 4 is opened, that between 1 and 2 closed, and steam introduced at the base of 4 instead of 1.

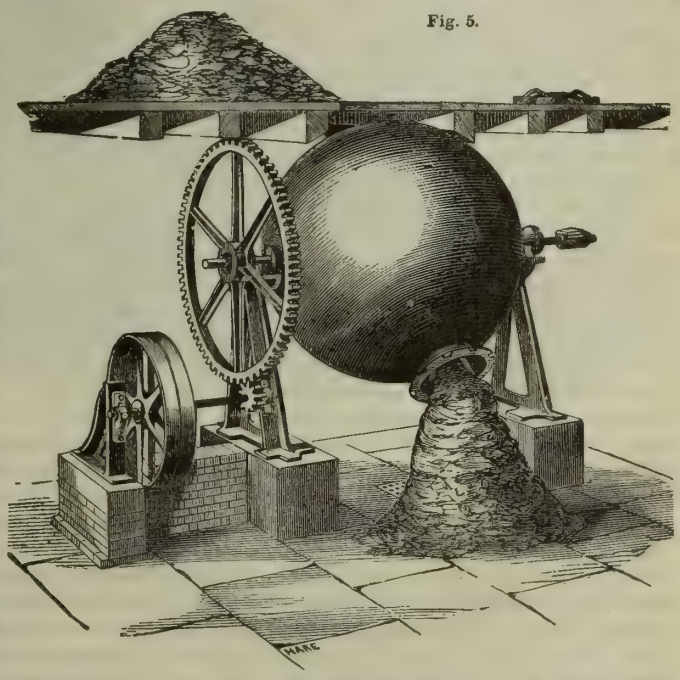
When high-pressure steam is employed, the cylindrical or spherical boilers above referred to are generally used. The artifice of giving motion to the boiler, in order to insure a thorough admixture of the rags and the liquor with which they are treated, originated in America, and was first introduced into England by Bryan Donkin & Co., in 1854.

Fourdrinier's revolving cylindrical boiler is shown in Figs. 3 and 4, the first of which represents a side elevation and part section, while the second is an end elevation. The two bearings are hollow, and at each end of the interior of the boiler are four perforated pipes fixed upon a bonnet, for the admission of clean and the escape of dirty water; and the jacket is perforated by one or more man-holes, and suitable openings for the introduction of water, steam, or alkali. The whole is caused to revolve by a spur wheel.

Bryan Donkin, & Co.'s spherical boiler is shown at Fig. 5. It is usually about 8 feet in diameter, or of such a size as to treat from 1 to 1¼ ton at once, and its spherical form renders it capable of sustaining a pressure which would be unsafe in a cylindrical boiler made of the same quality of iron; the form is, moreover, convenient, as it facilitates the removal of the rags at the end of the operation, it being only necessary to rotate the boiler without the lid. It is caused to rotate, by the gearing to the left of the engraving, about three times in two minutes, and during its revolution lifters inside agitate the rags. The trunnions are hollow in order to admit of the introduction of steam, water, or the alkaline lye, and they are carefully turned to avoid cemented or run-lead joints. The dirt and refuse are removed during the process of washing by strainers within the boiler. It is usual to introduce the unboiled rags through a hole in the floor above, the boiler being placed in a vertical position and the lid removed. Another form of boiler, manufactured by Roeckner & Co., of Newcastle-on-Tyne, is shown in Fig. 6. As will be seen, an oval-shaped boiler is placed in an inclined position, and is caused to revolve in such a direction as that the worm elevates the rags while steam is introduced at the lower end; during the washing water enters at the top. It is capable of operating on about 5 tons of rags per week.

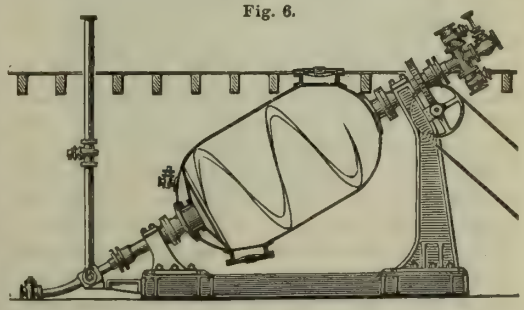
For boiling moderately soiled rags Planche recommends the following:—For 500 parts of the rags take 6 parts of carbonate of soda (indicating 80° on the alkalimeter), and 3 parts of unslacked lime, and dissolve the lime by sprinkling it with a little water, and then mix with soda. Boil the whole three or four hours in from 60 to 100 parts of water. A precipitate of carbonate of lime is formed, and free caustic soda remains in the solution.

Fig. 5.



Iron boilers are objected to, however, in some mills where the best qualities of paper are made, on account of the fact that small particles of iron rub off and discolour the paper. In these cases wooden vats with mechanical stirrers are preferred. The boilers of Messrs. Neyret, Orioli, & Fredel, consist of two vessels, one within the other, and the

Fig. 6.



heat is communicated to the mass in the inner vessel by steam circulating in the jacket so formed. This system has the advantage of preventing any condensation of steam in the lye, by which its strength is materially decreased.

It is hardly necessary to mention that a high pressure is desirable for coarse and strong rags, as this naturally implies a high temperature. When

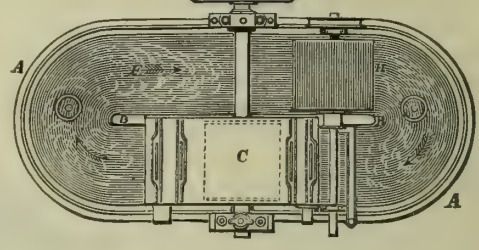
the finer class of rags are being treated a lower pressure is recommended, as it does less harm to the fibre.

Preliminary Washing.—Some manufacturers prefer to pass the stuff after it leaves the boilers through an apparatus whose sole function it is to remove the sand, &c., which it may contain; and although this additional process is seldom resorted to, at least in this country, it may be well briefly to describe the arrangement designed by Wrigley and Petrie for this purpose. It consists essentially of a long trough, provided with a finely-perforated false bottom. At one end is placed a washing cylinder, similar to that subsequently described as existing in the rag engine; and at the other end is an ingenious arrangement for raising the stuff (which is introduced automatically in the neighbourhood of the washing cylinder) from the water, with which the trough is nearly filled. A series of self-acting rakes carry the mass gradually through the water, and the thorough washing removes all sand and other fine particles, causing them to pass through the meshes of the false bottom. Fresh water is constantly supplied at the exit end of the trough, and the currents of water and rags thus travel in opposite directions; the stuff is delivered to the rag engine in a state which tends to the preservation of the cutting edges, in that it is freed from all particles of a gritty nature.

In other mills, again, the rags, after leaving the duster and before their introduction into the boilers, are washed with the same object in view. A very simple form of apparatus may be used, consisting of a rotating drum of wire gauze, immersed in a tub, at the base of which water is introduced under pressure; and as the drum contains the rags, they are thus held in suspension by the water, while at the same time they are prevented from escaping.

Washing and Rag Engines.—The apparatus into which the rags are now introduced—the washing engine—performs very important duties in the manufacture of paper. It more thoroughly cleanses the rags, and reduces them to what is technically known as "half-stuff." Many forms of apparatus have been devised from time to time for accomplishing this. Formerly it was done by what were known as "stampers" or "stocks;" but a great advance was made when, about the middle of last century, the *Hollander* was invented by the Dutch. The principle of this machine is still retained in the *Rag Engine*. Figs. 7 and 8 represent a plan and longitudinal section of a rag engine, but the details vary somewhat with different makers. The vessel, A A, 10 feet long, 4½ feet wide, and 2½ feet deep, is composed of eight metal plates (or it may be formed in one casting), bolted to a wooden foundation, and is provided with a division, B B, of such a length as to leave a trough of a uniform width round it. A cylinder, C, rotates in one trough, and may be driven either by toothed wheels or belt gearing. It is provided with a number of blades, arranged in pairs, and extending the entire width of the cylinder. C rotates immediately above a metal plate, *e*, *e*, which carries a number of steel blades firmly embedded in it. The fixed blades make a small angle with the axis of the cylinder, and the distance between

Fig. 7.



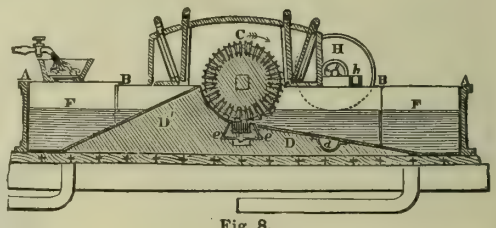


Fig. 8.

the two sets can be adjusted, by the aid of levelling screws, according to the degree of fineness desired in the resulting fibre. The cylinder, rotating in the direction of the arrow with a velocity of about 230 revolutions per minute, causes the water and rags to circulate in the engine, and the latter are necessarily subjected to the action of the blades. As a very thorough washing of the rags takes place, it is essential that fresh water be constantly supplied; the dirty water is, at the same time, removed by an arrangement which varies at different mills. Sometimes a cylinder, H, is arranged in the portion, F H, of the trough, and is caused to rotate either by the current of water or by gearing. When driven by gearing, it is formed of two discs of wood or copper, and covered with fine gauze, which allows the water to enter, but keeps back particles of the fibre. A number of buckets within this cylinder conduct the water to a trough in the axis of the drum, by which it is led away. The whole can be raised out of the vat when, as is the case in certain parts of the process, the removal of liquid is not required, or its height in the pulp can be varied at pleasure. In another form of cylinder a series of tubes are connected with a central hollow axis; this is connected with a long descending tube, external to the engine, and the cylinder is allowed to rotate under the influence of the current; the tube, therefore, provided it be initially filled with water, will remove the dirty water on the principle of the syphon. The peculiar shaped elevation, D D′, only exists at the side of B B, at which C revolves, and is technically termed the *mid-feather;* a trough, *d*, is usually cut in it, which is covered with a lattice, and is for the purpose of retaining sand and other heavy bodies.

Clean water is introduced from a trough or cistern, provided with means of preventing sand and other impurities from finding their way into the

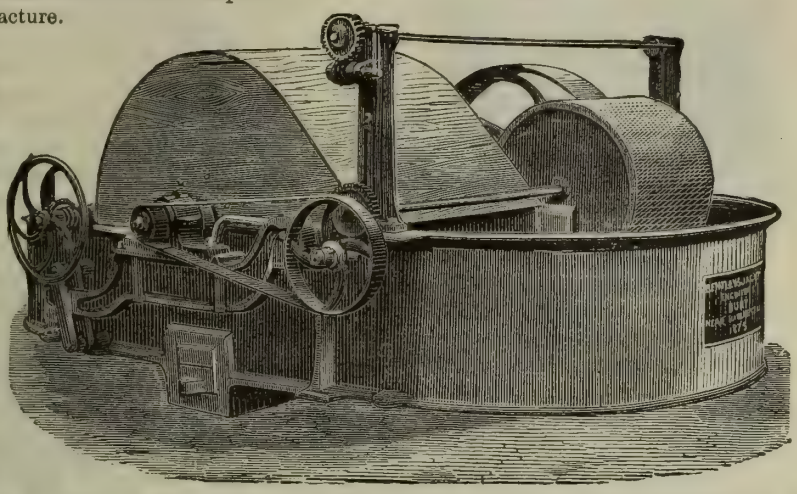
engine. It should be here noted that an abundant supply of pure water is very essential to the production of the finer qualities of paper, and this is the reason why the county of Kent and a few other localities on the chalk formation are so well adapted for this particular manufacture.

As regards the method of driving the engines, it may be mentioned that formerly toothed gearing was exclusively employed. Cog wheels with wooden teeth were replaced about the year 1820 by iron spur-wheel gearing; and this method enabled the manufacturer to drive four or more engines from one source of power, by continuing the line of shafting and spur wheels. Even with the small rollers of about 26 inches diameter the wear and tear on this system was very great; and it is quite inadequate to the driving of a number of large rollers, about 30 inches in diameter, such as are commonly used at the present day. When belt gearing is substituted for toothed wheels, which was first done on a large scale about thirty years ago by G. and W. Bertram, of Edinburgh, it is found that the rags are broken in a much more regular manner, and in a shorter time, as the rollers work more steadily on the plates than with any system of wheel gearing, and that the roller, bars, and plate last longer when not subjected to the vibrating action of wheel gearing. In several large mills recently fitted with belt gearing by the above firm the crank shaft of the engine (compound) is considerably elongated, and carries the same number of driving pulleys, 9 or 10 feet in diameter, as there are engines to be driven. The steam engine revolves at an uniform rate of about 70 revolutions per minute, and any number of rag engines is thus driven by the use of a single spur wheel. The pulleys keyed on the roller shafts are about 3 feet 6 inches or 4 feet in diameter. As an illustration of the economy of power on this system, it may be mentioned that at one mill, where only steam power is employed, 2 tons 15 cwts. is the entire consumption of coal required to produce 1 ton of paper; and the power obtained by employing only one steam boiler suffices to work eight "beaters," which produce sufficient stuff to keep a 102-inch paper-making machine (such as that described further on) at work night and day; this represents the production of no less than 30 tons of paper in a week.

An incidental advantage of the belt system consists in the facility with which the beating rollers can be lifted at *both* ends of the spindle; whereas when the toothed gear is employed it is necessary to lift at one end only, and the vibration is so great that the lifting gear requires to be constantly undergoing repairs.

Fig. 9 represents a general view of a rag engine,

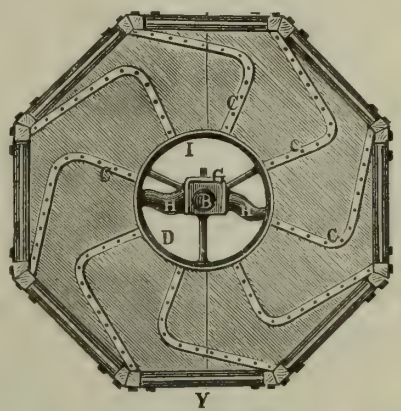
Fig. 9.



with its accessories, as manufactured by Bentley & Jackson, of Bury, near Manchester. It is provided with a washing cylinder, as already described, which is driven by a belt from the main shaft of the roller; and by means of the lifting gear shown in the diagram, can be adjusted to the required position in the pulp.

Figs. 10 and 11 represent transverse and longitudinal sections of Hammond's form of washing

Fig. 10.

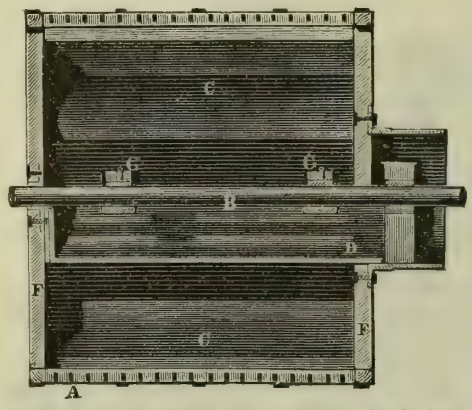


Y

cylinder, which consists of an octagonal drum, F, of a solid construction, and covered with fine wire gauze. It is divided into eight compartments by the scoops, C C C; and the lower portion, D, of the inner tube consists of a hemi-cylinder, which is suspended freely by arms, H H, and bearings, G G, from the axis, B. Externally to the drum a tube, I, is attached, within which D rotates. If now the drum be caused to rotate so that the scoops tend to elevate water, it will be seen that each scoop, on reaching the horizontal position, will discharge its contents into the trough, D, whence it will be led away through the

external portion, I. It is hardly necessary to add that all friction at G G must be avoided, as this would

Fig. 11.



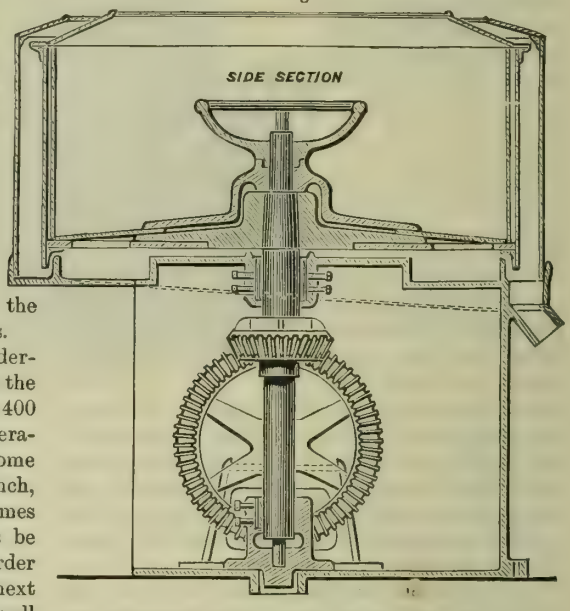
cause D to discharge its contents back into the scoops, and nullify the action of the apparatus.

As the dimensions of the rag-engine vary considerably, the amount treated at each operation is not the same in different mills, but in England from 300 to 400 lbs. is a usual amount. On first commencing operations, the roll, C (Fig. 7), should be set at some distance from the fixed knives, nearly half an inch, and gradually brought nearer as the fibre becomes disintegrated. It is necessary that the particles be reduced to a certain extent in this process, in order to prepare them for the bleaching, which next takes place. This result may be attained either all in one engine, or the rags, after being partially reduced, may be transferred to a second engine on a lower level, where the preparation for bleaching is completed. All the engines through which the pulp passes up to this stage are technically known as *breakers*, and when it leaves them it is known as *half-stuff*.

Bleaching may be accomplished either by the use of chlorine gas or of a solution of bleaching powder, or by both these methods combined. It is necessary before the bleaching commences that the pulp be drained, in order that it may be more permeable to the bleaching agent. Although in some mills draining vats are employed, they occupy a large space, and various forms of apparatus have been designed for conducting artificially this operation. The older form consisted of a tub, having its sides perforated, and provided with a piston. When the contents of an engine had been introduced, the whole was subjected to pressure, and subsequently torn into shreds by iron picks; but by this method one main object of the draining—namely, the obtaining of a spongy mass—was defeated. On a second system the pulp is formed into a kind of moist board, and then coiled into rolls, thus exposing a considerable surface to the action of the bleacher. Unquestionably, however, the best artificial process consists in employing a revolving drainer, in which case the moisture is very thoroughly removed by centrifugal force.

Fig. 12 represents Torrance's patent drainer, as made by J. Bertram & Son of Edinburgh, which, however, is principally used for draining pulp after the bleaching operation. It consists of a perforated cylindrical box inclosed within a fixed case, and caused to revolve at about 250 revolutions per minute. It is capable of treating about 4 cwts. in half an hour.

Fig. 12.



When the wet process, known as "sour bleaching," is resorted to, the chlorine solution is generally prepared in cisterns lined with lead, or covered with a thick coating of white lead. The hypochlorite of lime is ground with two or three times its weight of water, the heaviest particles are allowed to subside, and the supernatant liquid is transferred to a cistern; this operation is repeated several times, and the final residue, consisting of sand, carbonate of lime, &c., is thrown away. On an average 100 lbs. of chloride will produce about 1 gallon of solution, the exact amount of course varying with its quality.

The vats employed are about 17 feet long, 8 feet wide, and 2 feet deep, and capable of containing from 5 to 15 cwts. of half-stuff. The solution having been added (to the amount of about 2 per cent. in the case of white, and from 7 to 10 in the case of coloured rags), sulphuric acid, diluted with about fifteen times its weight of water, is usually added, in order to facilitate the liberation of the gas. The details of the process may be varied to a great extent; but the following will give a general idea of the order in which the several operations take place:—

The requisite volume of chlorine solution is added, and after a definite interval the sulphuric acid is introduced. When the chemical action has nearly ceased, the greater portion of the liquid, considered as spent, is allowed to drain away, and fresh solution, but no acid, is added. The amount of this second

addition will depend on the colour and general character of the rags.

In some mills the sour bleaching is conducted in the rag-engine itself, and in this case a quantity of the solution is pumped in, the motion of the engine being maintained; but, of course, the addition and withdrawal of water being stopped. When the bleaching of the pulp has been carried to the requisite extent, the whole is drawn off into another and considerably larger engine, called the *poacher*, whose function is to thoroughly wash the pulp, and remove all traces of the bleaching liquid; and as it is not required further to reduce the pulp, it is not provided with knives as in the former case. When washed, the pulp passes from this to vats provided with perforated bottoms, in order that the water may drain away.

When bleaching is performed by the aid of chlorine gas, this is conducted from the generator by means of large leaden pipes to the top of the vats, which contain a quantity of the pulp dried by one of the methods already described. The vats are formed of masonry covered with a coating of pitch, and they are about 16 feet long, 5 feet wide, and 4 feet deep, the whole being covered with flagstones. Arched chambers are also at times employed. Finally, it is the custom in some mills to spread out the pulp on wooden trays, which are then introduced into the chlorine chambers.

The amount of gas required varies considerably with the nature of the rags; but it is calculated that 1000 lbs. of pulp (free from water) require from 50 to 140 cubic feet of gas for their treatment.

The introduction of gas is stopped as soon as the chamber is found to be full, and it is gradually absorbed by the pulp; the whole is then transferred to a washing engine, which is at times provided with bronze in place of iron blades, as the latter would be attacked by the hydrochloric acid contained in the pulp.

The bleaching by means of gas frequently takes place in the same drainers that are used for bleaching by solution. The latter method is, however, usually preferred; as in addition to its being extremely disagreeable to work with the gas, it is found to act with great violence on the half-stuff, entirely destroying some of the finer fibres before the bleaching of the coarser ones can be completed. Its use is nevertheless recommended for the coarser class of paper.

Chlorine gas prepared in the ordinary way by acting on binoxide of manganese and common salt with dilute sulphuric acid, or binoxide alone with hydrochloric acid, is always contaminated with a small quantity of hydrochloric acid; and as this is injurious to the pulp fibres, it must be removed either by passing the gas through water, or by causing it to pass over pieces of the binoxide, which require renewal from time to time. The purified gas then passes into the chambers, as above explained.

The complete removal of the chlorine by washing is an extremely tedious process, and as its presence would be very detrimental in the subsequent processes, an *antichlor*, usually hyposulphite of soda (protochloride of tin, arsenious acid, sulphite of soda, or sulphate of lime might also be used), is added, as it forms soluble compounds with the chlorine present. Although the repeated washings after bleaching involve a considerable additional expense to the manufacturer, it is nevertheless to his interest that they be carefully gone through, as otherwise the acid formed will cause a brownish tint in the paper produced. The antichlors help towards the formation of such acids. Thus, when sulphite of soda is used, the sulphite liberates sulphate of soda, common salt, and sulphurous acid, as the following formula indicates:—

$$2Na_2SO_3 + Cl_2 = 2NaCl + Na_2SO_4 + SO_2$$

and as these are liberated throughout the whole mass of the pulp, only the most perfect washing can entirely remove them.

M. Gauny has proposed to bleach pulp by means of bichromate of potash. For 100 parts of dry pulp he recommends 50 of bichromate and 150 of hydrochloric acid, mixed with a sufficient quantity of water to make the pulp float. After standing for twelve hours the chloride of chromium is washed out by means of clean water, and the pulp treated with a small quantity of bleaching powder to insure a perfect white. The chloride of chromium having been precipitated by an excess of lime, the mixture is calcined in a reverberatory furnace, and converted into chromate of calcium. We are not aware, however, that this method has been ever carried out on an extensive scale, and it would apparently be very costly.

Beating or Refining.—When the washing has removed as much as possible of the chlorine from the pulp (since it would be very injurious both to the machinery through which it subsequently passes, and to the paper ultimately produced), the mass is drained, and usually passes to an engine called an intermediate engine, similar in general arrangement to that already described, but having the knives both on the roll and mid-feather blunt, though carefully adjusted, in order to rub the half-stuff to a finer condition, while the remaining portions of chlorine are being removed. On leaving this the pulp is caused to run into the beating or refining engine, of which there are various forms; but the oldest is similar in all essential particulars to the ordinary rag engine, the principal difference being that there are more blades on the rolls, and the velocity of rotation is greater. When a colour is to be imparted to the paper, the necessary colouring matter is added to the pulp at this stage.

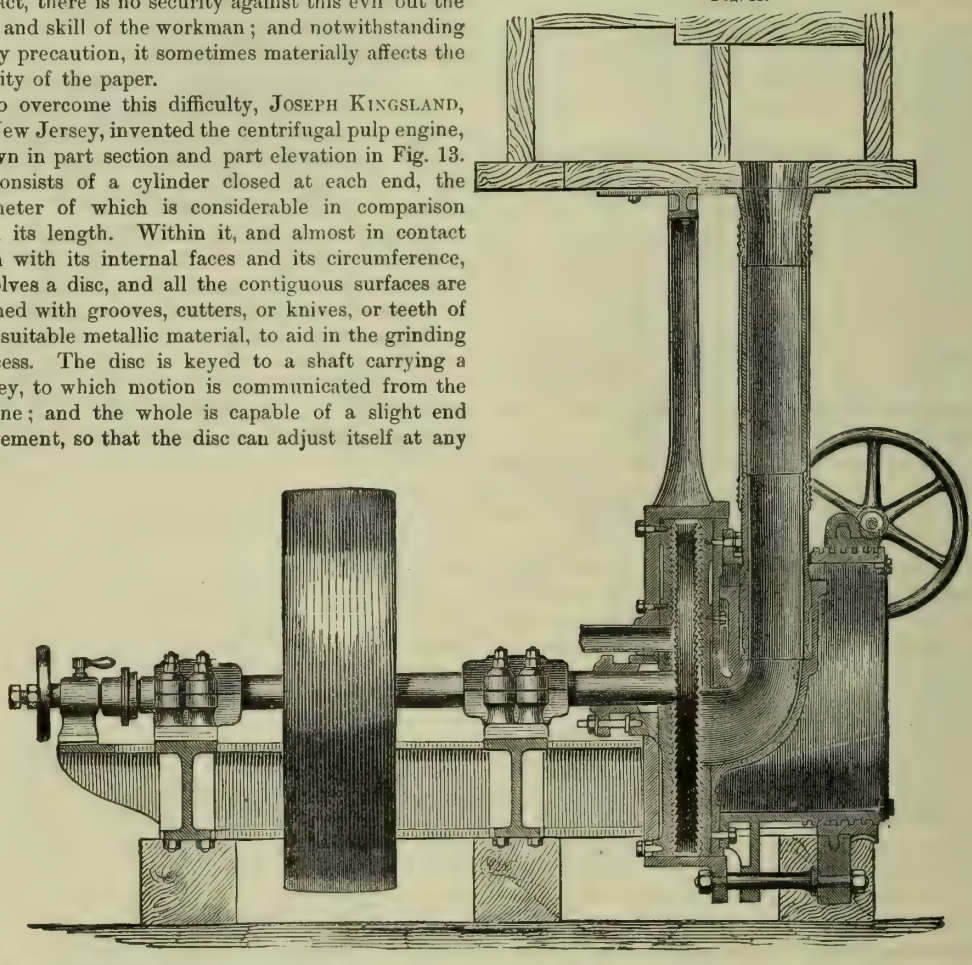
A modification, whereby the current is induced in the beating engine by a supplementary paddle or elevator, has been introduced by Debie, Granger, and Pasquier. A drum, carrying a series of curved blades, rotates near to the face, D′ (see Fig. 8), of the mid-feather (which is made of a form to suit it), and in close proximity to the cylinder, C. In rotating it raises the pulp, causing it to fall between the fixed plate and cylinder, the current thus takes place in

a direction opposite to that in the ordinary form of engine.

The principal defect of the beating engine arises from this, that while a certain quantity of rags is put into it for the purpose of being ground to fibre or pulp, these rags are not of the same tenacity; and being kept under the action of the grinding process for three or four hours, the weaker rags are reduced to a finer pulp than those of a stronger texture. Also, one engine may be emptied into the reservoir already containing pulp of a longer or shorter fibre. In fact, there is no security against this evil but the care and skill of the workman; and notwithstanding every precaution, it sometimes materially affects the quality of the paper.

To overcome this difficulty, Joseph Kingsland, of New Jersey, invented the centrifugal pulp engine, shown in part section and part elevation in Fig. 13. It consists of a cylinder closed at each end, the diameter of which is considerable in comparison with its length. Within it, and almost in contact both with its internal faces and its circumference, revolves a disc, and all the contiguous surfaces are formed with grooves, cutters, or knives, or teeth of any suitable metallic material, to aid in the grinding process. The disc is keyed to a shaft carrying a pulley, to which motion is communicated from the engine; and the whole is capable of a slight end movement, so that the disc can adjust itself at any

Fig. 13.



carry the particles to the periphery when at the front, it tends to check their escape at the back; and as this checking effect is greater on the larger particles, they are, of necessity, subjected to a greater amount of attrition, and consequently there is a tendency to bring all the pulp to the same degree of disintegration on leaving the engine. The extent to which the pulp is thus disintegrated depends of course on the closeness of the teeth, the amount of feed, and the velocity of rotation of the disc; and the rate at which the pulp is supplied may be varied by increasing the distance between the reservoir and the engine. This arrangement is said to be specially serviceable when large quantities of one class of paper are required, as it gives great uniformity of pulp, occasions a moderate loss of material, and is rapid in its action.

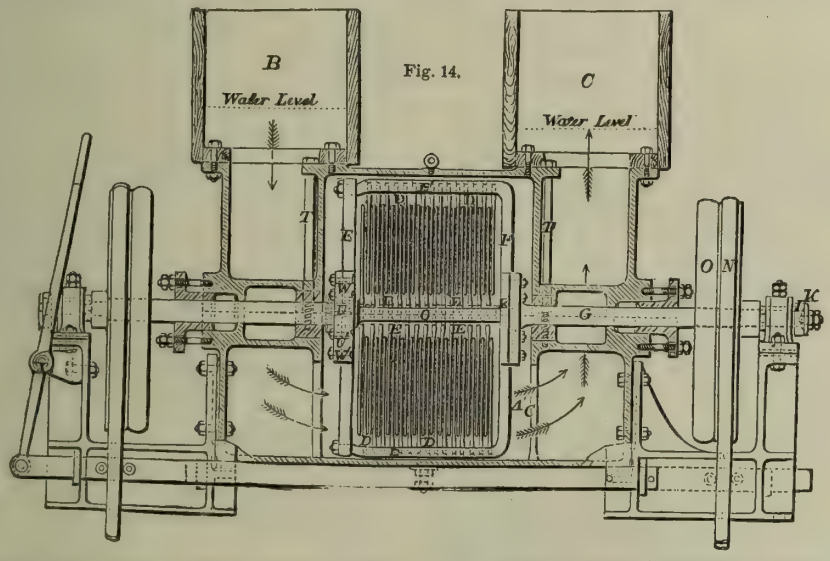
Modifications in the general construction have been introduced into this machine by Stuart, the principal of which consists in fixing the exit pipe in such a manner that its distance from the axle of the disc can be varied, in order to increase or decrease the period during which the pulp remains under the action of the grinding surfaces. Several serious defects of the ordinary engine are avoided by this form of apparatus, as it provides for withdrawing the fibre at the moment at which it is sufficiently acted upon; and as the rate at which the stuff is intro-

required distance from either internal face of the drum, and the length of this path is regulated by set screws. The "stuff," together with water, is introduced from a vat, elevated about 4 feet above the engine, and entering the drum near its centre, is gradually conducted to the periphery by the motion of the disc. It then passes round to the back, and on approaching the centre, escapes by the discharge pipe into a suitable receptacle. It will thus be seen that while the centrifugal force of the disc tends to

duced into the engine is independent of the motion of the grinding disc, the rate of rotation of this latter may be varied at will. It will be further noticed that the slight longitudinal play above referred to enables the grinder to adjust itself to various kinds of stuff; thus in case a knot of fibre enters, the disc at once moves towards the opposite end of the cylinder, the knot passes more freely towards the periphery, during which time it is reduced in size; and the feed is, at the same time, diminished by the partial closing of the exit pipe, so increasing the amount of grinding action to which the knot is subjected. It will also be evident that, in the case of easily reduced fibre, the mass will flow readily through the engine, and the disc will remain almost in the middle of the cylinder, thus increasing the amount passed through to a maximum; when tough fibre is under treatment, the exit pipe will be partially closed, thus proportionately increasing the amount of action to which the stuff is subjected. As the rate of flow, with a given position of the disc, depends solely on the height of the liquid column, and as this latter is regulated by altering the position of the exit pipe radially, it is evident that the rate of flow can be varied at will by such an adjustment. By means of a hand wheel, seen at the right of the engraving, a screwed cylinder, carrying one of the internal grinding faces, can be moved in such a manner as to vary the distance between the two fixed grinding faces according to the nature of the stuff under treatment.

The above pulper, though producing a thoroughly even and continuous supply of pulp, is found to exercise a peculiar cutting action on the fibres; and the following form, known as Cowper's pulper, avoids this objection; and as it opens and separates the fibres rather than cuts them, it is peculiarly suitable to the treatment of pulp from wood, straw, and Esparto grass. It is seen in longitudinal section in Fig. 14, and consists of a closed cylinder,

Fig. 14.



T T, provided with openings at its opposite ends for the introduction and escape of the pulp. A frame, F F, carrying bars, D D, and nearly filling the vessel, T T, is caused to revolve by motion communicated to the shaft, G, provided with fast and loose pulleys, N O, and with an arrangement at K whereby a slight longitudinal adjustment can be given to it. The shaft, Q, carries bars, E E, which pass closely between D D, the distance between the two sets being varied at pleasure by the arrangement at K. Q has no such appendage, but is provided with fast and loose pulleys. The rate of flow depends on the difference of level of the liquids in B and C, and may therefore be varied at will. The two shafts, it need hardly be added, move in opposite directions, so that the bars produce opposing currents, thus dragging the fibres apart, and exercising no cutting action on them.

The pulp is made long or short according to the quality of the paper. Newspapers, which require strength, are made of long pulp. Writing paper, or paper of a fine texture, is made of shorter pulp. Indeed the quality of the paper depends very much on the manner in which the pulp is prepared in the engine. If the cutting edges are brought together too rapidly the fibre is cut, and produces a tender paper; and owing to the porous nature of this paper, the sizing, whether for printing or writing, will be weak. The stuff should be what is called *mellowed* in the engine, and this is effected by a judicious working of the roller, not lowering it suddenly, or much at one time, on to the plate; but equally and gradually, until the pulp is ground as fine as is required. This is generally attained in three and a half to four hours, after which the pulp is caused to pass through a valve from the engine to a *pulp vat*, which is large enough to receive the contents of several engines. The arrangement of this vat, and its connection with the paper-making machine, will be presently described.

Engine Sizing.—If the pulp prepared as described were converted direct into paper, it would be found to have a porous surface, causing the ink to run,

and would, in fact, be blotting paper, quite unserviceable even for printing purposes. It thus becomes necessary to introduce some size, such as gelatine, into its substance, and it was early proposed to do this in the beating engine. Gelatine, however, could not be so employed, as any excess not adhering to the pulp itself was at once lost in the water. A resinous soap, or combination of resin with an alkali, was therefore added, and this being decomposed in the engine, by the addition of alum, left the fibres in a condition for producing a properly sized paper. Resinous size is now made as follows:—Soda, showing 80° on the alkalimeter, having been dissolved in water, is rendered caustic by the addition of a little lime, the exact amount of this depending on the strength of the first named salt, as shown by the alkalimeter. The liquid is shaken, and the supernatant solution introduced into a tub at the temperature of boiling water. Powdered resin having been added, the whole is stirred for two or three hours, when it is run into a receiver. A portion of the resinous soap so produced is, when required for use, introduced into water heated by steam, and a quantity of starch mixed with lukewarm water is also added.

It is occasionally found possible, and even advantageous, to size some of the commoner qualities of paper by adding thoroughly pulverized resin to the contents of the rag engine; but the method requires considerable judgment in practice. Sizing by means of resin, however, can only be applied to the commoner qualities of paper, and when a good writing surface is desired it is still necessary to employ gelatine. In this latter case, the machine-made paper is caused to pass through a tub containing the sizing liquid, after its actual manufacture has been completed. This method will be explained more fully in its proper place. Resin is precipitated from its solution by means of alum; this, therefore, is added to the mass, either in the solid form, or preferably as a solution of known strength, obtained by dissolving the crystals in water at about 65° C.; a double decomposition takes place, and a combination of resin and alumina with sodium sulphate is formed.

The details of the sizing process vary considerably among manufacturers; but the following may be taken as about an average, as used for common writing and printing papers:—

Per 100 Parts of Dried Pulp.	
20 to 30	parts of starch
10 to 12	" resin
10 to 12	" alum.

And to the sizing solution are usually added from 30 to 50 parts of kaolin, as presently to be explained. When a colouring matter is present on which alum would have a prejudicial effect, this is usually replaced by about one-third of its weight of sulphate of zinc.

Many mineral substances have from time to time been added to paper stock, principally to increase its weight; and in 1858 Sholl took out a patent for adding carbonate of lime, a substance which, however, had long been fraudulently used in order to increase the weight; but he found it to have the property of fixing the ink in the pores of the paper, thus rendering it immovable.

But the only really useful addition is kaolin or China clay, or some similar aluminous compound, as it attaches itself to the fibre, and, while giving the requisite opacity and a good surface, takes both printing and writing ink well, and has the advantage, from a manufacturer's point of view, of increasing the weight.

It has been proposed that small quantities of glycerine be added to the pulp in order to give the paper greater flexibility, and especially to give copying paper the quality of taking up colour readily. It was expected that the necessity for damping paper prior to being printed might thus be obviated; but the experiments have not been very successful.

M. Canson patented the following method of sizing, in which the resin usually used is replaced by white wax. The wax soap is prepared by dissolving 0·5 kilo. of wax in 1 litre of a solution of caustic soda marking 5° on Beaumé's hydrometer, and the mixture boiled till the wax is dissolved, when the whole is introduced into about 30 or 40 litres of boiling water, and 3 kilos. of potato starch, thoroughly mixed with water, are at once added. The mixture is stirred till it thickens, and may be preserved for a fortnight in a cool place. When used, the mass is introduced into the engine containing 30 kilos. of (dry) pulp, and the requisite quantity of water, and when the whole has become thoroughly mixed, from 300 to 500 grams. of alum in solution are added.

Colouring. — Any desired shade of colour may be imparted to a paper by one of the following processes—

1. By intermixing with the pulp some insoluble substance, such as smalt (a sort of glass coloured by cobalt) or ultramarine.

2. By adding a coloured liquid which simply stains the paper.

3. By using rags which are already coloured about the required shade, and, of course, omitting the process of bleaching.

4. The best plan consists in employing two substances which, when combined, give the requisite tint. The first having been caused to combine thoroughly with the pulp, the addition of the second at once produces the required colour. In this way the common buff shade is obtained by using sulphate of iron and an alkaline solution.

The following list, given in Hofman's exhaustive treatise on the "Manufacture of Paper," includes all the substances of importance which are used by the paper-maker for imparting colour to the paper; and by their means, either alone or mixed in the proper proportions, all colours are produced—

Prussian blue.
Ultramarine.
Indigo blue.
Aniline blue.
Aniline red.

Pink, or cochineal red.

Brazil wood (which imparts either a fine red or an orange-brown colour, according to the treatment it has undergone).

Logwood (for violet colours).

Chrome yellow or orange.

Orange mineral.

Sesquisulphate of iron.

Copperas.

Venetian red.

Yellow ochre.

Quercitron, or Oak bark.

Nutgalls.

Lampblack.

To these should be added "smalts," a finely pulverized and levigated glass coloured blue by oxide of cobalt; it has, however, fallen into comparative disuse since the discovery of a method for artificially producing ultramarine.

Blue.—The coarser class of paper used for packing is made of rags blued by indigo, which, when reduced to a pulp, are not subjected to the process of bleaching. The finer class of papers may receive a blue colour in a variety of ways. Formerly "smalts," as just mentioned, was principally employed; but it is now largely replaced by artificial ultramarine. Prussian blue may also be used, and it is usually produced directly in the beating engine by adding 95 parts of sulphate of protoxide of iron and 100 parts of yellow cyanide of potassium. For the best class of papers smalts is preferred to ultramarine, as the colouring imparted by it is more lasting.

Yellow.—The pulp may have a yellow colour imparted to it by adding chromate of lead while in the engine, or this may be actually formed there by decomposing the carbonate, chloride, or sulphate of lead by means of red chromate of potassium, in the proportion of about 4 parts of either of the former to 1 part of the latter.

Red or Pink Red.—A carmine may be obtained by the following process:—Boil for half an hour—

1000	parts of	crude cochineal
16	"	soda (Alicante)
39,000	"	water.

Then remove the vessel, and add

50	parts of	pure alum
10	"	cream of tartar.

The liquid is now stirred, decanted, and the whites of four eggs added after they have been well beaten; and if the carmine does not appear on the surface in flakes the mass should be heated. The decanted matter is then thrown on a cloth, and dried at about 30° C. The carmine obtained will be about one-twentieth of the weight of cochineal taken; and if the decanted liquid be boiled, and again treated with the whites of four eggs, half this quantity of carmine of an inferior quality will be obtained.

Buff.—To colour paper light buff, a mixture of 5 parts of sulphate of iron and 3 of soda (occasionally replaced by 2 of chloride of lime) is employed, each salt being brought separately to a state of solution; or these salts may be thrown direct into the rag engine. When a darker shade is required, 16 parts of sulphate of iron and 9 parts of soda (replaceable by 6 parts of chloride of lime) are used in a similar manner.

Green is obtained by mixing yellow and blue dyes, in proportions depending upon the shade required. Ultramarine is used for the fine, and Prussian blue for the commoner qualities of paper.

Brown.—By the use of umbers, ochres, &c. Chloride of manganese may be saturated with carbonate of soda and filtered, and the product becomes brown on the addition of chloride of lime.

All the shades of colour required in paper-making may be obtained by mixing in different proportions two or more of the three primitive colours—blue, red, and yellow, with or without the admixture of black, in order to adjust the shade.

The principal colours used for this purpose are—

Blue.—Cobalt and ultramarine.

Yellow.—Chromate of lead, already referred to.

Red.—Ferric oxide, vermilion, brazil wood, and madder red.

Black.—Lampblack, purified from its greasy particles by caustic soda or potash, and subsequently washed.

Preparation of Pulp from Materials other than Rags.—Among the very numerous materials which have been proposed as substitutes for rags, whether entirely or partially, in the manufacture of paper, the most important are, as already stated—straw, wood, and Esparto grass. The preparation of these is to a certain extent analogous to that of rags, already described; but differs, especially in the case of wood, in several important particulars, and it will be well to describe these in some detail.

Straw.—As early as 1801 Matthias Koops obtained a patent for the manufacture of paper from straw; but he employed it unbleached, and a white paper was not obtained from it till 1841. A good and economical method for working straw was not, however, devised till 1851, in France; and the present method is based upon the one then patented by MM. Coupier and Mellier. The following is the method adopted by them:—The straw, after having been cut into small pieces by a chaff-cutting machine, is subjected to the action of a boiling solution of soda or potash, of from 7° to 10° Beaumé (1·051 to 1·075). It is then put into a tub provided with a perforated false bottom, through the cover of which vessel a pipe enters, terminating in a rose head; the other end of this pipe reaches nearly to the bottom of a closed iron vessel, capable of containing 60 or 70 gallons. Into this latter the alkaline solution is introduced, and kept boiling by high-pressure steam traversing a spiral tube. A slight escape of the steam within the vessel causes the solution to traverse the pipe, and passing through the rose head, to fall in streams on the vegetable matter in the tub. The iron vessel is refilled after all its contents have been forced through in this manner, and the operation repeated until the tub contains 30 or 40 gallons of solution for each cwt. of vegetable matter present. A second pipe con-

nects the base of the vat, or *kier*, with the base of the iron vessel; the tap, which closed this during the above operation, is now opened, and the mass of liquid is caused to circulate between the two vessels for about nine hours, when it is drawn off by a third pipe, and the above process repeated with water in place of the alkaline solution. After this the contents of the vat are washed with cold water. They are now transferred to another vessel to be bleached, by mixing with a solution of hypochlorite of alumina, in the proportion of about 20 or 25 parts of the latter to 100 of the former; 70 gallons of water also being required for each cwt. of vegetable fibre. This "half-stuff," which has a good colour, is now thoroughly washed with boiling water, transferred to a beating engine, and converted into paper, either alone or mixed with rag pulp.

The process now generally adopted for the preparation of straw pulp differs but slightly from that to which rags are subjected, and may be divided into the following operations:—

Cutting.—The straw after being examined is cut, usually by means of machines similar to the rag cutters already described, into short lengths, and the cut fragments are sometimes allowed to fall on a wire grating, to which a slight shaking motion is communicated in order to free it from grain and other impurities.

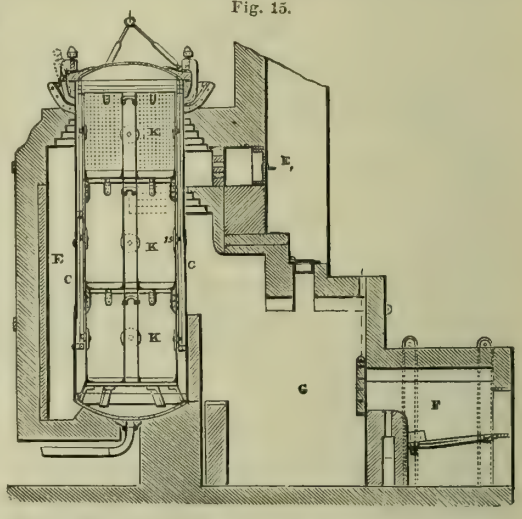
The short lengths are then introduced into a suitable boiler, similar in all respects to those already described, and treated with a lye of caustic soda. This may be made by mixing 788 lbs. of soda-ash of 93 per cent. with 637 lbs. of caustic lime. These are dissolved in hot water, and after the sediment has settled part of the liquor is drawn off, and more water added to the lye in order to reduce its strength.

In the earlier experiments the straw was treated in open vessels, and frequently by lime alone; but it was soon found that a high pressure is necessary in order to completely disintegrate the straw, and render soluble the silex which coats it, as well as to break down knots, &c. This is the only point in which the treatment of straw differs materially from that of rags.

Edward A. Cowper patented in 1872 considerable improvements in the apparatus for boiling under pressure, whereby both time and fuel are saved. He adopts the device of feeding the boilers by means of iron boxes containing hot soaked straw, or whatever is to be operated upon, thus avoiding all cooling down of the boiler. Fig. 15 represents, in section, the form of boiler with its setting. The boiler, C C, is set in brickwork in a vertical position, and the heat of a furnace, F, placed at a distance to avoid damaging the sides of the boiler, is communicated through the flues, G E, the chimney being placed at E_1.

The wood or other fibrous substance having been packed in boxes, such as K, K, K, these are arranged in a circle in a large soaking vat, kept hot, where the lye permeates through the substance of the material. A crane transfers them as required to trucks to be conveyed to the boiler, into which they are introduced while still hot by a second crane provided with a

Fig. 15.



spring catch. When the hot caustic solution has been introduced the lid is hermetically closed and the boiling allowed to progress. A space is left down the centre to allow a free circulation of the liquid.

Washing.—The straw pulp is thoroughly washed after its treatment with soda lye, as any alkali remaining would cause a loss of chlorine in the subsequent bleaching. This washing takes place either in a washing engine alone, which should be provided with a smooth bed-plate and blunt blades on the cylinder; or prior to passing through such an engine it may be treated in a vat provided with a false bottom, which is covered with bagging or coarse matting. The pulp is now passed into either drainers or stuff chests.

The *web machine* into which straw pulp is frequently introduced from the stuff chest consists of a screen, forming cylinder, and web felt, such as are used in the cylinder paper-making machines described at page 539. By the use of it the costly sorting to which the straw would, in the first instance, have to be subjected, is in great measure avoided.

The pulp is now ready for bleaching, and this process is usually conducted in the engine in the same manner as for rags; a considerably greater proportion of bleaching powder is, however, found necessary—from 15 to 25 parts of bleaching powder, and a corresponding quantity of sulphuric acid, being used for each 100 parts of paper when this is made solely from straw; and this quantity has to be still further increased when an insufficient quantity of soda lye has been used. Several processes for bleaching have been patented from time to time, the principal object in view being the economizing of soda lye, but none appear to have come into general use.

It is unnecessary to subject the pulp to any further reduction in a beating engine, for the fibres are generally so far reduced in the above operations that, after the chlorine has been removed, and the necessary size and colouring matters been added in

a beating engine (not provided with cutting edges), they can be conducted direct to the paper machine. This is similar in all respects to that described presently (see page 535), except that it is often found necessary to replace the iron press rolls usually employed by some of wood, in consequence of the excessive adhesion between the straw pulp and metal. India-rubber has also been used for this purpose.

Treatment of Waste Paper.—It will only be necessary briefly to refer to the several processes connected with this subordinate but very important operation.

The collecting and sorting is conducted in the same manner as in the case of rags, the number of subdivisions being nearly as numerous. The paper is first passed through a duster, whereby, in addition to dust and impurities being in great measure removed, the pieces are separated from each other and reduced to a convenient size for the sorters. All but the worst qualities are boiled with soda, in order to extract printing ink; water alone would suffice for writing ink. A stationary boiler is preferable for this purpose, as motion, however slight, cannot fail to separate a large part of the extremely fine fibres, which thus get lost in the wash water, a large quantity of which is necessary in order to remove the black liquid resulting from the removal of ink. Tubs provided with false bottoms are generally used for the boiling process, the heat being communicated to them by waste steam. The mass, in the form of a large cake, is removed gradually to a washing engine with blunt knives, and here numerous fibres, threads, &c., make their appearance and cause considerable trouble, but they can in great measure be removed from the surface by a wooden rake. The pulp is then bleached, as already described, in the same engine; and the subsequent processes are precisely similar to those already explained in the treatment of rags.

Preparation of Esparto Pulp.—The raw material is first sorted by hand, and all roots and flowers removed, after which the treatment is identical with that of straw. It is, however, introduced direct into the boiler without there being any necessity for *breaking-down*, as in the case of straw. The boiling usually takes place in vomiting tubs, similar to those employed for waste paper in some mills. They are provided with false bottoms on which the material rests, and steam is introduced below. A pipe rises from the centre of the false bottom, and the liquid being forced up this is distributed in a spray over the surface. The solution of soda is similar to that employed when straw is operated upon.

Mr. Joseph Carbonnell, of Paris, adopts the following process:—200 lbs. of "raw" Esparto is placed in a wooden vat, and 20 lbs. of alkali and 30 lbs. of quick lime are mixed with it, and the vat immediately filled with cold water until the Esparto is covered. The contents are then kept at boiling temperature for four hours by means of copper pipes in the vat, which are perforated with a number of small holes for steam to escape and mix with the contents of the vat. The liquid is then drained off, and the Esparto placed under a hydraulic press. It is afterwards mixed with clear cold water in an engine similar to those used in triturating rags.

After fifteen minutes of trituration the grass is reduced to a fibrous matter: 24 lbs. of chloride of lime dissolved in clear water are then introduced, and the cylinder turned in order to thoroughly mix the mass.

In another vessel, lined with lead, $1\frac{1}{4}$ lb. of sulphuric acid (marking 66 per cent.) are mixed with 3 lbs. of clear cold water. This liquid is by degrees added to the pulp, which immediately assumes a reddish colour, but at the expiration of 45 minutes becomes perfectly white, and the pulp is ready for the paper-maker.

Voelter's Process for the Mechanical Treatment of Wood.—As early as 1756 Dr. Schaeffer of Bavaria proposed to make paper from sawdust and shavings by mechanically forming them into a pulp; but the process could not be worked profitably with the machinery at his command.

H. Voelter in 1860 patented (in England) an arrangement whereby a number of pieces of wood were converted into pulp by pressing them against a grindstone. He has since taken out patents in 1865 and 1873.

The several appliances through which the material passes, as shown in Fig. 16, may be thus briefly described:—A is the pulping apparatus, consisting of a vat, K, in which the stone, S, revolves, the blocks of wood being held against it by P P; water is introduced at G, and the rotation of the stone carries the pulp against a screen, E, through which the finer particles pass. The portion failing to do so is led by the trough, F, to the first refining cylinder, B, previously passing through an oscillating basket, which retains the coarser portions. From this it is led through a distributing apparatus and hopper, C, to be uniformly supplied to the refining cylinder, D—these cylinders being of the usual construction, and covered with fine sieves. That portion which fails to pass through is transferred by an elevator to the mill-stones, E, of the ordinary construction, and after leaving them is joined by the fine fibres which passed through E (Fig. 16). The whole now enters a mixing reservoir, F, whence it is thrown on to the cylinder, G; the pulp which passes into this is distributed on to a similar cylinder, H, and the contents of this again pass to the last cylinder, I, which differs from the others in being surrounded in its lower portion by an impervious leather jacket, so that the pulp ascends in order to enter it. The reader who requires further information with regard to this apparatus is referred to the two specifications of 1860 and 1865; Nos. 3182 and 3041 respectively.

Chemical Processes for the Treatment of Wood—The processes which have been devised for obtaining pulp from wood by chemical means may, according to M. Schützenberger (in Wurtz' "Dictionnaire de Chimie"), be conveniently divided into the two following classes:—(1) Those in which the wood is

treated by sulphuric or hydrochloric acid at the normal pressure, with a subsequent cleansing by means of steam. (2) Those in which caustic liquors, especially soda, are employed at a high pressure.

Sinclair's Method.—The wood having been cut up into pieces about 1 inch broad, one-eighth inch thick, and from 2 to 3 inches long, is introduced into a boiler, and a solution of caustic soda, in the proportion of 600 gallons to 10 cwts. of dry wood, is poured over it. The boiler having been firmly closed, the heat is raised till a pressure of about 180 or 200 lbs. on the square inch is attained, when the fire is withdrawn and the boiler allowed to cool, after which the lye is blown off, the top door removed, and the contents scalded. The discharge door is then opened, and the pulp transferred to a poaching engine to be washed with pure water; when the resin, &c., are easily removed and the clean fibres obtained, which are said to be longer and firmer than those produced by any other method. This method is also very economical, both as regards the actual working and the setting up of the necessary plant. That required for the production of 10 tons of pulp weekly costs about £1200, and can be worked by four men of ordinary skill. The entire cost of producing 1 ton of pulp is said to be £15 5*s.*, the expenses being distributed as follows:—

	£	s.	d.
43 cwts. of wood at 30*s.* per ton,	3	4	6
Caustic soda, for boiling the above, at 14*s.* per cwt., and employing 28 lbs. per cwt. of wood (partly recoverable),	7	10	6
Bleaching liquor,	3	0	0
Labour of cutting wood,	0	4	0
Fuel, 15 cwts. of coal, at 8*s.* per ton,	0	6	0
Labour of boiling, washing, and bleaching,	1	0	0
Total,	£15	5	0

Aussedat's Process.—In this extremely simple process, the wood is disintegrated by the action of a jet of vapour. In one end of a cylindrical high pressure boiler, about 4½ feet in diameter and 10 feet high, is fixed a false bottom, so that the wood placed on it may be removed from the liquid resulting from steam condensed in the chamber. The whole is mounted on lateral bearings, which serve for the introduction of the vapour, and the wood is introduced through a man-hole at the upper end. Taps exist at the upper and lower ends for the removal of the liquid and any uncondensed vapour that may be present. The wood having been introduced, the jet is *gradually* turned on, in such a manner that at the end of three or four hours the temperature corresponds to 5 atmospheres—that is, about 150° C., at which point it is maintained for an hour. As the slightest contact between the wood and the condensed water would at once discolour the former, it is essential that the water be removed from time to time by one of the outlets provided for the purpose.

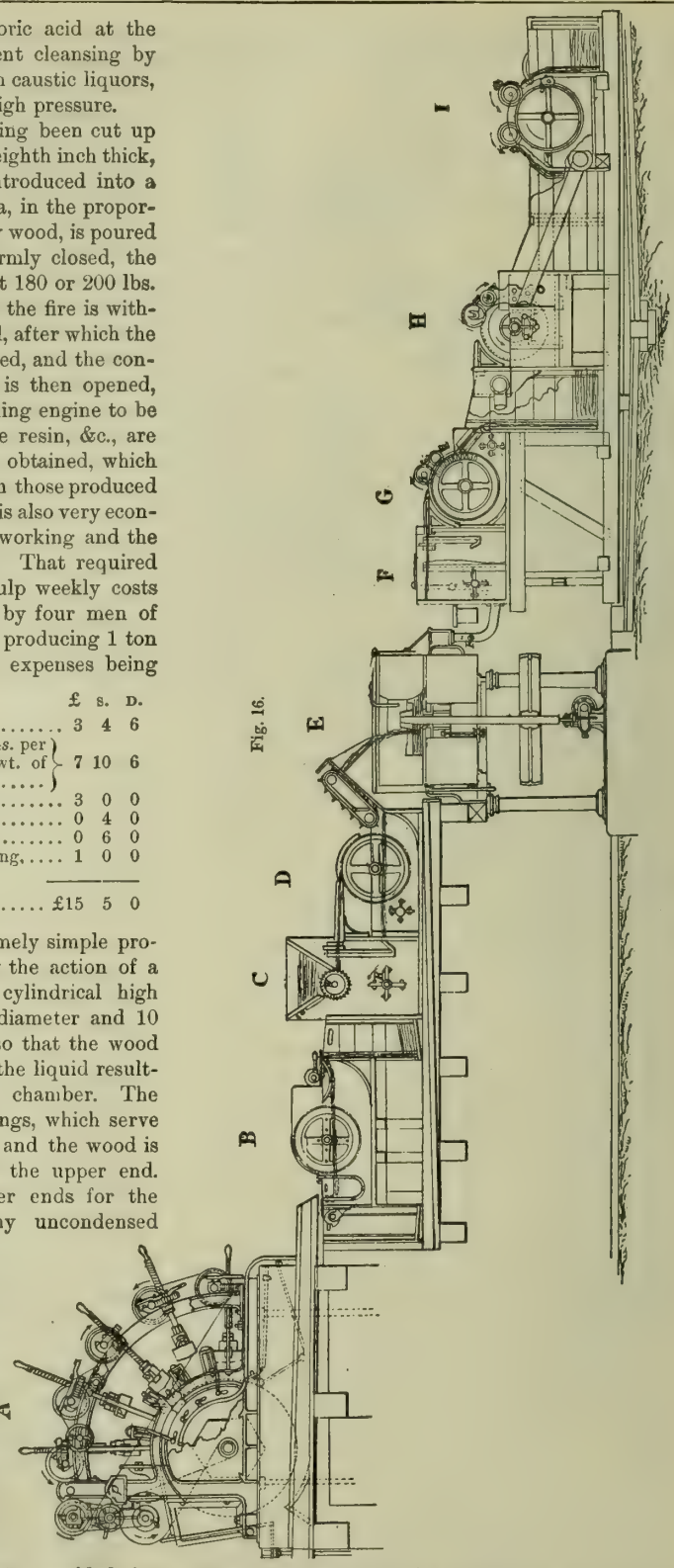


Fig. 16.

The above treatment is suitable for all kinds of wood; and although the usual practice is to intro-

duce it in the form of logs about a yard long, any waste, such as chips, shavings, &c., may be treated. Although not necessary, it is preferable to remove the bark; but all rotten wood may be left, as it is removed in the condensed water.

The logs, after being thus subjected to the action of the steam, whereby the fibre is disintegrated, and the sap, as well as all matters of a gummy or resinous nature, are removed, are cut up by any suitable means into discs, the thickness of which is about 1 inch, more or less according to the nature of the fibres required. They are introduced into a breaker, acting on the principle of an ordinary coffee mill, and by this means are converted into half-stuff, which, after being mixed with a suitable quantity of water, is passed through mills provided with conical stones, in order to reduce it to whole-stuff.

The pulp thus prepared is principally employed in the manufacture of the best qualities of card board, especially such as are used by artists, since the light brownish shade which it always possesses is found to improve the tone of the colours, and is, at the same time, very agreeable to the eye. According to Bourdillat, the above treatment by vapour has a chemical as well as a mechanical action; for, in addition to the vapour traversing the cellular tissue of the wood and dissolving a considerable portion of the cell contents, acetic acid is disengaged by the heat, and this assists the vapour in its action on the internal substance of the wood.

Keegan's Method.—The wood used is soft deal or pine, and it is sawn up into pieces from 6 to 12 inches long and half an inch thick. The pieces should be all of the same size, and the smaller they are the more rapid is the operation. They are placed in a cylindrical boiler, which turns upon a horizontal axis during the maceration. In a second boiler is prepared a solution of caustic soda, of about 20° Beaumé (1·161); and this is introduced through a tube into the first boiler, which is subsequently closed hermetically, and the soda is forced into the pores of the wood by means of a pump. A pressure of 50 lbs. on the square inch is sufficient when the wood is not more than half an inch thick, and the injection is completed in half an hour, after which the superabundant solution is pumped back into the second boiler for the next operation. When the excess of solution has been thus removed from the wood, steam is introduced between the double sides of the first boiler, and the temperature of the wood raised to from 150° to 190° C. The wood is then washed in the ordinary way, till the water running off it is perfectly limpid; and the half-stuff thus produced may be converted into pulp either before or after bleaching, according to the quality or colour of the paper to be produced.

The process of Bachet-Machard, belonging to the first of the classes above alluded to, was devised with a view to saccharify the wood, and then to obtain pulp as a bye-product in the distillation of alcohol; but, in practice, the amount of the latter produced is found to be of secondary importance. The wood, cut into discs about an inch thick, is introduced into vats, each of about 200 cubic feet capacity, and the interstices are filled in with a mixture of 1 part of hydrochloric acid to 10 of water, when the mass is left to stand for eighteen hours, during which period the heat is raised. Each charge produces about 18 cwts. of dried pulp, and requires 600 lbs. of acid for its treatment. After being carefully washed to remove traces of acid, the discs are reduced to pulp in the manner adopted in Aussedat's process. It can be partially bleached with profit, and employed in the manufacture of inferior qualities of paper, either by itself or mixed with other stuff. A method has, however, not been devised for thoroughly bleaching it at a moderate cost.

At Poncharac, near Grenoble, a somewhat dangerous process is employed for the disintegration of wood. It consists in adding *aqua regia*, composed of 94 per cent. of hydrochloric acid and 6 per cent. of nitric acid, to the wood contained in vessels of about 20 cubic feet capacity, formed of burnt clay; the mass is allowed to stand for about nine hours. No less than 60 parts of acid are required for each 100 parts of wood. The process is sometimes modified in such a manner as to admit of heat being applied, when the consumption of acid is considerably diminished.

It has also been proposed to treat the wood with hot ammonia in closed vessels, caustic soda being subsequently added.

M. Tessié de Montag proposes that the wood, after treatment by an alkaline lye under pressure, should be bleached by means of manganate of sodium. The lignin, or incrusting matter, dissolved in the alkali could then be deposited by a current of carbonic acid, and the regeneration of the alkali would thus be effected at a moderate cost.

According to M. Fiztier, the usual caustic might be replaced by sulphide of sodium, which would act in an analogous manner, and could be regenerated with facility; for it would only be necessary to evaporate and calcine the lye, the organic matter would be destroyed, and the alkaline sulphide would be at once recovered.

Paper from Bamboo.—The following information relative to the manufacture of pulp from bamboo is derived from a paper published in 1876 by Mr. Routledge, who, it should be added, was the introducer of Esparto as a material for making paper. He is of opinion that this new material will prove as superior to Esparto as that is preferable to straw, and he proposed the following process of manufacture:—The young and fresh cut stems having been passed through heavy crushing rolls, are passed through a second series of rolls, which are channelled in order to thoroughly split and partially divide them, when they are cut into suitable lengths by any convenient means, and delivered to the boiling pans. Both the boiling and washing processes are conducted in a series of pans similar to Coupier's boilers already described, and the lye of

caustic alkali can thus be re-employed until exhausted; and when the extractive matter contained in the fibre is rendered sufficiently soluble, the washing is proceeded with in a similar manner, hot water being employed. The mass, having been rinsed with cold water, is drained in presses, and placed in a "devil" or "willow;" here it is thoroughly "teazed" out, and assumes a tow-like appearance. After this has been dried by a blast of hot air, it is packed in bales for exportation, and only requires to be bleached and mixed with other stuff, or worked by itself, according to the nature of the paper required. The bamboo thus treated yields as much as 60 per cent. of its weight of fibre.

The inner bark of the bamboo has long been used by the Chinese for the manufacture of paper of excellent quality, which is celebrated for the clear and delicate impressions, called *India proofs*, which it takes from engraved plates.

Manufacture of Paper in Japan.—The inhabitants of Japan have been, perhaps, more successful than any other people in the simplicity of the means adopted for the manufacture of paper, and in the variety of uses to which it is applied.

In May, 1869, Lord Clarendon directed the attention of H.M. Consuls in Japan to the subject of paper manufacture. The reports of these gentlemen were presented to Parliament, and have been issued as a Parliamentary Paper, marked "Japan No. 4 (1871), Reports on the Manufacture of Paper in Japan." The following information is derived from these documents—

The fibre chiefly used in Japan for the manufacture of paper is that of the Paper Mulberry (*Broussonetia papyrifera*). This plant was introduced into the island about A.D. 610. Its average height is 6 feet, and cuttings for the manufacture are taken from it after the fifth year's growth. There are many varieties, and the fibres are selected according to the quality of paper to be made. The mulberry stalks being cut into lengths of from 2 to 3 feet are steamed, and the separation of the skin at the cut ends indicates that the steaming process is completed; and the bark is peeled off and used for the manufacture, the sticks being burned. The skins are dried by being tied loosely together and hung on transverse poles, and after this they are washed, by being left in running water for a day or longer. The inner fibre can then be separated from the outer skin, by drawing the slips of bark under the edge of a knife; and paper may be made of either the inner or the outer fibre; the former being for paper of the best quality. The process usually takes three or four days, but adepts can accomplish it in two.

Parcels of fibres, weighing about 32 lbs. each, are well washed and boiled, so that they are no longer glutinous; the water used is previously infused with the ashes of burnt buck-wheat husks. Stirring is continuously maintained, and the workman is assured of the completion of the process if, on withdrawing the stirring sticks from the bottom, the water wells up through the holes left by them, and spreads *evenly* over the surface. This even spreading of the water seems to be important; for to insure it a small quantity of common lime is sometimes added, although the colour of the resulting paper is slightly affected. To clear the fibre thus prepared from the ash with which it has been boiled, it is placed in a basket through which running water is allowed to percolate, until the residue of the ash infusion is thoroughly expelled.

The material is now to be "pounded." This is done by women, who handle sticks about 3 feet long and square in section, except at the handle. The pounding takes place on an oak or cherry wood table, and is continued for about an hour. A little rice paste is mixed with the fibre before pounding, or what is better, the prepared root of a plant called "tororo."

The mode in which paper cloth "warranted to wash" is made in Japan, is thus described:—Take some of the paper called "hôsho," or some of the best "senka," and dye it of the colour required. Boil some of the roots called "kon-niaku-no-dama," with the skins on. Try them with the inner portion of a rice stalk; when it penetrates easily, they are sufficiently boiled. Peel them, let the water run off, and then pound them into a paste. Spread this paste on either side of the paper, and let it dry in the sun till quite stiff. Then sprinkle water upon it till it is thoroughly damp, and leave it in that state for a night. The next morning roll it upon a bamboo, of the thickness of the shaft of an arrow, and force it with the hands from either end into a crimple in the centre; unroll it, and repeat this process two or three times, rolling it from each side and corner of the paper. Then crimple it well in the hands by rubbing it together till it becomes quite soft, and then sprinkle water on it again to damp it. Pull it out straight and smooth, fold it up, and pound it with a wooden mallet. It may then be put into water as much and as often as is desired without sustaining injury, having become a strong and lasting material. Boxes, trays, and even sauce-pans may be made of this cloth, and sauce-pans thus manufactured sustain no injury over a strong charcoal fire. Bags may be made of it, in which wine may be put, and heated by insertion in boiling water. Paper thus prepared may be used for papering windows, and without being oiled will withstand the rain.

Papermaking by Hand.—The sheet of paper is made by a mould, composed of a frame covered with fine wire-cloth, having a movable edge called a *deckle*. This mould the workman dips into the vat containing prepared pulp, lifting a portion of the pulp on its surface. The water flows through the wire cloth, and leaves the fibre on the top. The workman then removes the deckle, and passes the mould to another, who turns it over, and presses it on a felt, to which the sheet adheres; the mould is then returned to form a new sheet.

About 130 sheets are laid in alternate layers of felts and sheets, and the whole submitted to powerful pressure. The sheets are then taken out of the

felts, and being laid together, are subjected to another pressure, after which they are parted or turned over, to prevent their adhering to each other. The paper is then taken to a drying house, and hung up on lines to dry. It is next sized, gently pressed, and the sheets parted from each other and hung up a second time to dry in a loft or drying house.

There are only a few vats working in this country, generally in the manufacture of paper in which great strength is required.

History of the Paper Machine.—The paper machine had its origin in France. Louis Robert was the first who appears to have conceived the idea of making a continuous web of paper on an endless wire-cloth, to which a rotary motion was communicated, thereby producing a web or sheet of indefinite length.

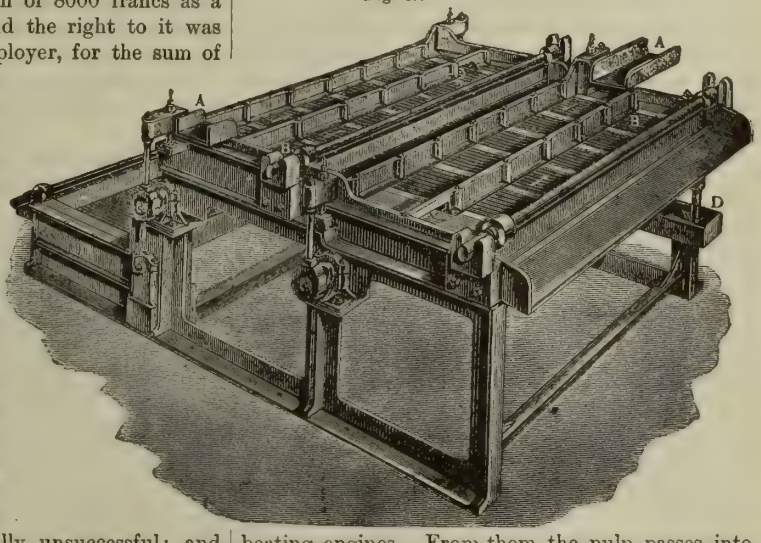
About the year 1798 Robert constructed a small model of a machine, by which he could make a narrow continuous strip of paper. Subsequently a machine was constructed by which paper 24 inches wide could be produced. The French government presented to Robert the sum of 8000 francs as a reward for his invention, and the right to it was purchased by Didot, his employer, for the sum of 25,000 francs. In England Messrs. Fourdrinier adopted the invention, and with the help of Bryan Donkin they in three years succeeded in constructing a machine which made a continuous web of paper; but after three years more of immense labour, and an expenditure of £60,000, the patentees found that their machine still required extensive alterations and improvements. They therefore applied to Parliament for an extension of their patent for fourteen years. The application was, however, owing to certain technical difficulties, practically unsuccessful; and thus this valuable invention, on which Messrs. Fourdrinier had expended so much, became public property, and largely benefited all, except those who had been so instrumental in its introduction.

Present Paper Machine.—The preparation of the pulp having been completed in the beating engine, it is all collected in the stuff chest, or reservoir (see Plate I.), in a condition to be delivered to the machine as required. The stuff chest is formed of wood or iron, and is usually capable of containing 1000 to 1200 lbs. of pulp. Within it a vertical shaft, carrying two horizontal agitating arms, each extending nearly across the vat, and provided with a large bevel wheel at its upper or lower end, is driven by a pinion on a horizontal shaft; it rotates from one to three times per minute, according to the quality of the pulp. An important desideratum in paper is *uniform thickness*, and this can only be obtained by a regular supply of pulp of uniform consistency, and a regular speed in the machine.

The following description of the several portions of the machine refers in great part to the engraving (Plate I.), which represents a very elaborate machine of the most modern construction, and for which we are indebted to Messrs. G. & W. Bertram, of Edindurgh. Such an apparatus (known as a 102-inch machine) is capable of producing the finest quality of printing paper, in a strip 94 inches wide, at the rate of 150 feet per minute, or 30 tons and upwards per week.

Sand Tables.—The pulp, on leaving the stuff-chests, passes through the *regulating box*, an appliance which has the effect of keeping a regular supply of pulp on the machine; and when it has been delivered by the stuff pumps, is mixed with a certain quantity of water drawn from the pulp immediately preceding it, and this mixture is then made to pass along sand tables, or spouting, in order to free the stuff from any gritty matter which may accompany it from the beating engines. From them the pulp passes into the strainer, an appliance which has in recent years been very materially altered in construction.

Fig. 17.



The *Knotting Machine*, or *Strainer*, was invented by Ibotson, an English paper-maker, in 1830, and is very essential for the production of the better class of papers, as by its means the knots or impurities are removed from the paper stuff or pulp, thus avoiding all irregularity in the paper produced, as well as the great waste of pulp that formerly took place. The knotting machine has been now brought to so high a state of perfection, that the pulp flows from the vat to the machine with perfect uniformity of substance.

Fig. 17 shows two of Ibotson's strainers as at present constructed. The pulp, enteting at the inlets, A A, passes in the directions indicated by the arrows; and the finer portions, filtering directly through the strainers, pass to the lip near B, whence they are distributed evenly on the machine. All

knots, lumps, and impurities are driven by the current through the openings at the end of the first strainer, opposite to that at which they enter; and after traversing in like manner the second strainer, B, they enter a pipe conducting them to the outlet trough, D, by which they are carried to an auxiliary strainer, C, placed on a lower level at the back of the apparatus. The movement of the pulp is facilitated by a jogging motion communicated to the strainers, by means of small ratchet wheels keyed on shafts, passing beneath the machine; and when various qualities of pulp are treated it is necessary to vary the size of the perforations in the strainer plates; they are, therefore, usually made movable, so that the plates can be changed when requisite.

More recently, however, it has been found advantageous, especially in the manufacture of the finer class of writing and printing papers, to replace the above flat jog knotting machine by revolving strainers, accompanied by a separate knotter. The engraving (Plate I.) shows the arrangement introduced by G. & W. Bertram in plan and elevation.

The pulp is delivered from the sand tables into the patent knotter, whence it passes into three vats containing the square revolving strainers, each of which is about 18 inches square and 7 feet long, and its four sides are covered with brass strainer plates perforated with extremely fine slits. The strainers, which are caused to rotate by suitable gearing, contain india-rubber bellows, worked at a high speed by pistons, and the fine pulp is thus drawn within the strainers, all knots, &c., remaining in the vat. The purified pulp then passes out through a hollow bearing at the opposite end of the strainer to the piston, and its escape is so regulated by a sluice as to keep the pulp in the vat at a height suitable for the working of the revolving strainer, which moves at the rate of about three turns per minute. It will be evident, that as they reject any stuff not properly beaten, such as strings, &c., these substances in time would accumulate in the vats, and thus prevent the proper action of the apparatus, were it not for the knotter above referred to.

It should be mentioned, that in revolving strainers constructed by J. Bertram & Son the use of india-rubber bellows is avoided, and they are replaced by a perforated tube about 7 inches in diameter running the whole length of the strainer, the holes in which are so graduated as to distribute the suction evenly within the strainer. The suction is effected by means of a pump, placed outside the vat, working very rapidly with a short throw; it is connected by a gland to one of the hollow bearings of the strainer itself.

The Endless Wire. — The pulp on leaving the strainer passes into a vat, containing a horizontal agitator or "hog;" here it is properly mixed and made ready to flow on to the endless wire cloth, which (in the machine illustrated) is 102 inches wide and 35 feet long. It is so supported by brass tube rolls as to render the layer of pulp absolutely uniform, thus insuring a constant thickness in the finished paper. The meshes of these wire cloths are extremely fine; in some cases there are as many as 19,000 holes per square inch; but the principal meshes employed are from 2000 to 6000 per square inch, and the ends are united so as to form one continuous sheet.

Below the tube rolls is the *save-all* — a shallow box which receives the water as it flows through the wire cloth from the pulp: for a large quantity of water is necessary in order to float the pulp along the sand tables, through the strainers, and on to the wire cloth. The pulp being partially freed from water, a slight side shake is communicated to the wire frame for the double purpose of getting rid of water and weaving the fibres of the pulp together before the water has, to any great extent, left it, the *deckle straps* keeping the pulp to the width required by forming ledges near the sides of the web. These bands or deckles are often made of a number of layers of cotton, gummed and sewed together, being about 1 inch in width and half an inch thick; more usually, however, they are made of vulcanized india rubber. They travel along with the wire, one on each side, and by their flexibility remain in contact with it, keeping the sheet any required width. They are guided by a frame which stretches across the machine, resting on its framework; and the breadth of pulp is regulated by widening or narrowing the frame.

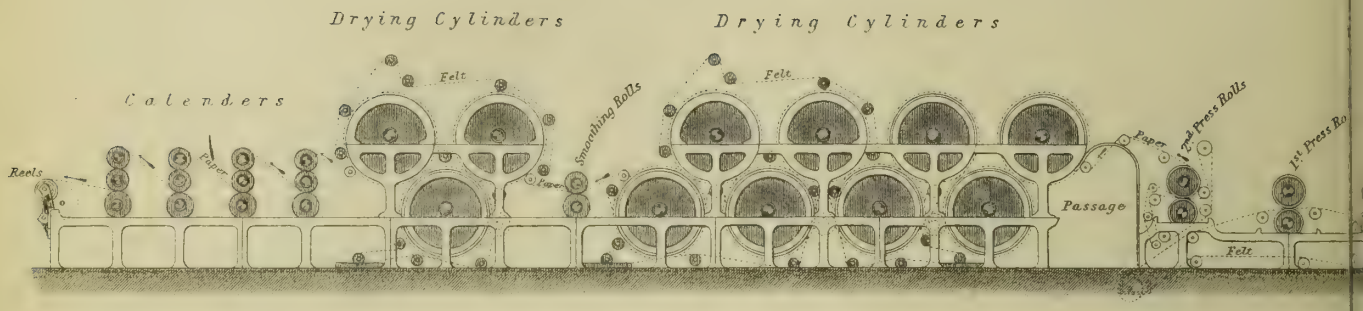
The Dandy Roll.—Travelling with the wire, the pulp passes to the dandy roll, which is simply a cylinder, the two ends of which consist of brass hoops fixed on a shaft, and having wires extended between them; or it is sometimes formed of perforated copper, and is covered with fine wire cloth. It is generally 7 inches in diameter, and corresponds in length to the width of the wire upon which it rests. The journals of this roll turn in slits in two upright stands; one behind the machine frame and the other in front of it; but, as the roll actually rests with its whole weight on the wire, it revolves by the progressive motion of the latter, while the stands prevent it from participating in the lateral motion. This roll, by running on the surface of the pulp, presses out a great quantity of water, and renders the paper finer and closer in texture. It is also by this part of the mechanism that the water-mark and the lined appearance which paper often presents are impressed.

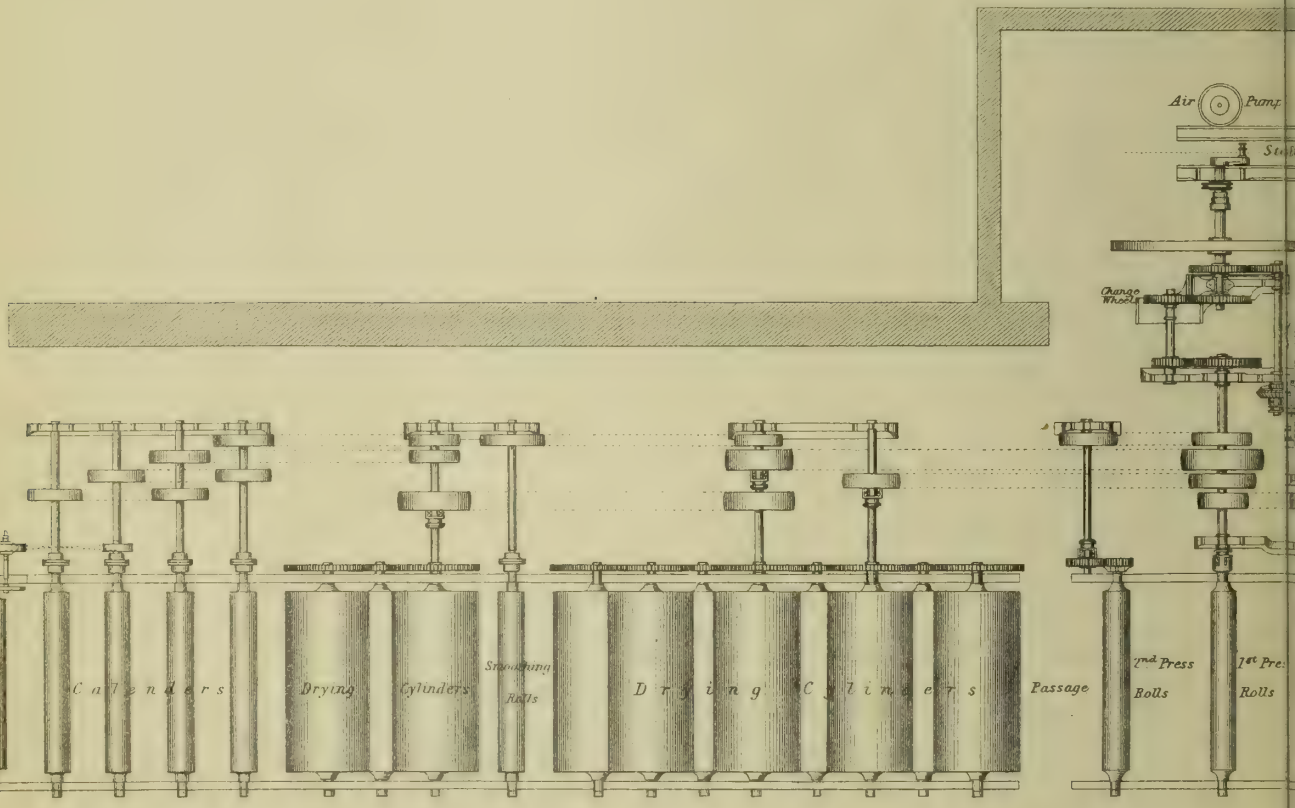
Suction Boxes. — Beneath the dandy roll, and across the machine, two suction or pump boxes are placed, open at the top. As the wire travels over these boxes, the action of the pumps with which they are connected draws the wire upon them with a pressure sufficient to make them air-tight, thereby extracting a large portion of the water which the pulp at this point still retains, and giving to it such a degree of consistency as fits it to bear without injury the pressure of the couch rolls.

The water so extracted, together with that collected in the save-all, is added to a fresh supply of pulp before it traverses the sand tables.

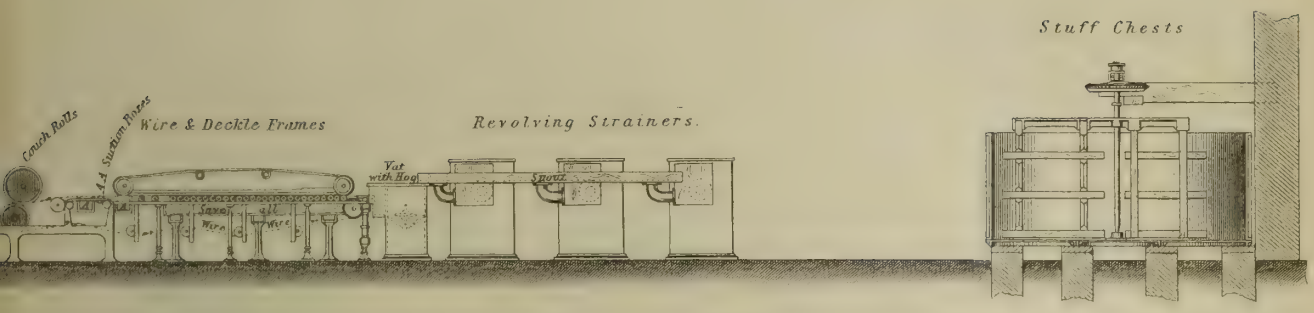
The Couch Rolls.—The web of paper now arrives at the couch rolls. These are two large rollers,

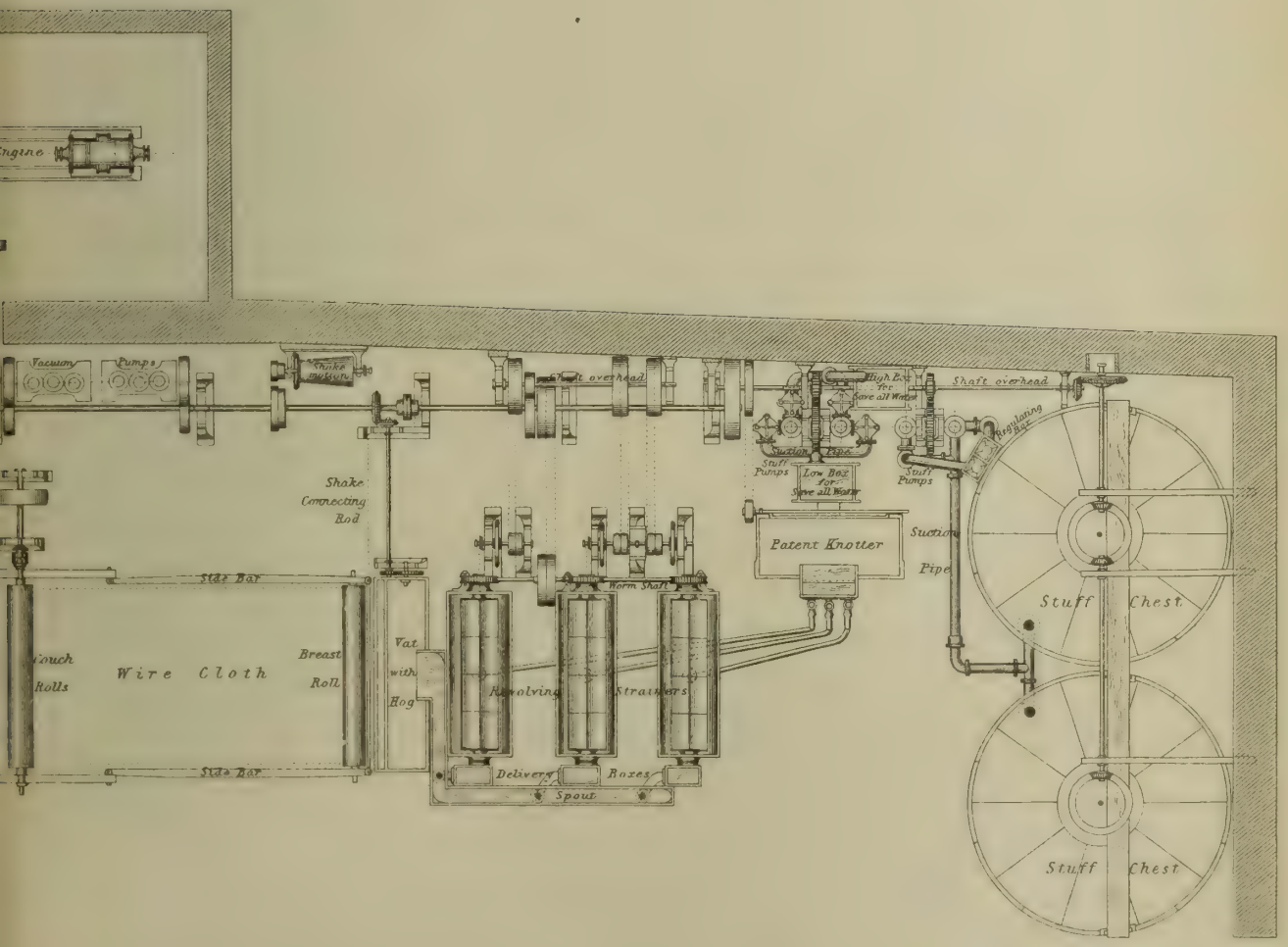
PLAN AND ELEVATION O





PAPER MAKING MACHINE.





usually of brass covered with felt. The under one revolves inside the wire, and gives the motion to it; the upper rests on the lower, and thus both wire and web of paper pass through between them, receiving a gentle pressure, which renders the paper still more compact, forcing out more of the water in it.

At this point the paper leaves the wire, and is received on a soft woollen blanket, or endless web of felt, revolving continuously on rollers; it is about 20 feet in length, and made with very great care.

Press Rolls.—This endless web carries the paper between two heavy iron rollers, called press rolls, which still expel a quantity of water. The paper can now bear its own weight, and may be handled gently with impunity. The sheet then passes through the second set of press rolls; but in order to bring the under side in contact with the upper press roll, it will be seen that the paper is inverted by being caused to pass underneath the second set of rolls, and thus these rotate in the reverse direction. This arrangement is necessary, in order to insure that the under side shall equal the upper in smoothness; for it is found that the wire and first press roll felt have a tendency to roughen the under side, while the upper surface is rendered smooth from being in direct contact with the roll. This second set of rolls is provided with an endless felt of its own, which, however, is usually made thicker and stronger than that employed in the first press rolls. Both felts are guided through their respective sets of rolls by means of the "felt rolls." It should be added that modern experience shows it to be better to work with all the above-named rolls cold, and not to heat them, as was formerly the practice. In some mills each press roll is provided with an arrangement for preventing the web of paper from adhering to the metal, and so passing round and increasing the diameter of the roll. These are known as *doctors*, and consist of strips of metal, or preferably vulcanite, held against the rolls by levers and weight, in such a position as to scrape the surface of the roll. The paper now passes to the drying cylinders.

Steam Drying.—For many years after the introduction of the paper machine, the paper, after passing through the press rolls, was wound on reels, cut into sheets by hand, and then hung up in the loft to dry. But in 1821 a very useful improvement was added to the machine by T. B. Crompton, who invented and patented a new mode of drying by heated cylinders and a cloth or felt.

Since that period the system of drying by steam has been brought to a high state of perfection, the number of cylinders being gradually increased, and the heat to which they are raised proportionately decreased; thus avoiding the evaporation of size which is sure to take place with rapid heating, but, at the same time, allowing of a very rapid speed being maintained. The drying cylinders are thus arranged in Messrs. G. and W. Bertram's machine. They are each 4 feet in diameter, and being eleven in number, afford a very large amount of drying surface; for it is essential that this operation be conducted gradually, especially at its commencement. Three of the first section of cylinders, having no felt on them, allow the moisture coming from the paper to escape freely; but the next five cylinders are provided with felts, which hold the paper against the heated surface, thereby smoothing and flattening it, and so making it the more fit for introduction between the smoothing rolls. These are highly polished cast-iron rolls, heated by steam; and as the paper reaches them in a slightly moist condition, they cause its surface to assume a fine smooth appearance. The paper now passes over the three last cylinders, all provided with felts, to render the contact perfect, and thus dry up any remaining moisture. By placing two of these below and one above the paper, its under surface is rendered more nearly equal to the upper. The arrangement here described is that adopted for the manufacture of the finest quality of printing paper.

Calender Rolls.—On leaving the cylinders the web passes through a number of rolls, the surfaces of which are very highly polished. In the machine shown they are arranged in four sets of three, but the exact system adopted is immaterial. The object of these calender rolls is to impart a finished glazed surface, the amount of this glazing, of course, depending on the number of rolls employed. They are ordinarily made of polished cast iron, as in the case of the smoothing rolls, but recently chilled iron rolls have been introduced. Considerable difficulty is experienced in preserving the high polish on the surface, and a suggestion is made in Ure's Dictionary that the surface should be electro-plated with nickel; but it has not, so far as we are aware, been acted on. It certainly would appear to be well worth a trial.

From the calender rolls the web is led to the *reels*, which are made of wood, and when an empty reel is placed in the machine it is caused to rotate with a greater circumferential velocity than that at which the paper is delivered, in order that a solid roll may be formed. To prevent the tearing of the paper owing to this extra velocity, a delicately-arranged "slipping motion" is introduced, and this being adjusted when the filling of the reel commences, the strain on the paper remains constant throughout the entire process. Provision is made on the machine for accommodating two reels, so that when one is full the other can be at once brought into action.

The full reels are now removed to another room to be cut to any size sheets required, one cutting machine being capable of cutting eight, or even more rolls at the same operation.

Cutting Machine.—Previous to the introduction of cutting machines, the paper was uniformly wound on a reel, the diameter of which could be diminished or enlarged, according to the size of sheet required. When the reel was filled, an empty one was put on, and the paper was cut off the full reel by hand. This method of cutting occasioned a great deal of waste; many attempts were therefore made to pro-

duce a machine which would cut the paper into sheets as it issued from the machine, or as it was wound off a reel; but most of the plans, after repeated trials had been made and considerable loss incurred, were laid aside as impracticable. J. B. Crompton appears to have been the first who produced a really useful cutting machine. About 1821 he secured a patent for cutting paper into suitable lengths by a pair of shears, as it issued from the machine; and in 1828 he again obtained a patent for cutting paper lengthwise by revolving circular blades fixed on a roller parallel to a cylinder. Finally, in 1849, Amos and Clark patented a cutter which obviated the difficulty that arose from the constantly increasing velocity of machines, causing the sheets to be cut into irregular lengths.

The first operation of this cutter is to cut the paper lengthwise into such widths as may be required. To effect this object, there are placed across the machine two shafts, armed with circular blades, which may be moved along the shafts to adjust them to any required width. These knives revolve at a much greater speed than the paper, which, as it issues from the machine, or is wound off the reel, passes between the two shafts, and is cut by the knives very exactly. It should be added that the knife on the upper shaft is larger in diameter than that on the lower, and as they revolve in contact, the action produced is similar to that of a pair of scissors.

The web being thus cut lengthwise, proceeds over a large drum to be cut across into the lengths required for the sheets. From the velocity with which it travels, this is a difficult operation, and requires the paper to be momentarily arrested in its course, at regular intervals, to admit of the sheet being cut square. With this view, the drum is so contrived as to have an alternating motion; at one time bringing the paper forward the required length, and then returning. This effect is produced by a crank arm, which can be adjusted at pleasure to regulate the length of the sheet. In front of this drum, at the point where the paper leaves it, is placed a solid board or wooden block, over which is suspended a movable board or presser. The paper passes between these, and when the drum has brought forward the required length of sheet, the presser, by a particular movement, is made to descend against the block, and holds the paper fast, while at the same instant a combined motion of rolls and levers brings a movable knife against a fixed knife, and the paper is cut in the same manner as by a pair of shears. The sheets immediately on being cut are caught by boys, and laid straight in handfuls. The drum, after bringing forward the required length, immediately travels back, while the pressers prevent the paper from being pulled along with it. Three rolls covered with felt are placed on the top of the drum to assist in bringing forward the paper, and the moment it is held fast in the pressers these rolls are raised by a lever and connecting rods, so that the paper is left loose on the drum, which by this arrangement can turn back without dragging the paper. The latter is continuously passing between the knives, and while the drum is making its backward motion, a *dancing roll* takes up the slack of the paper.

The apparatus is invaluable in cutting laid paper on which is a water-mark. As this water-mark requires to be in the centre a portion of the machinery can at any time be stopped by hand, and a small part of the sheet cut off, thereby bringing the water-mark again to its proper place, if, through any cause, it happens to get displaced.

A very useful form of paper cutter is now generally adopted, in which the paper from six or more rolls is cut simultaneously into sheets of any required dimensions. It is found to be much preferable to use some such appliance rather than cut the paper at once on leaving the machine, for a six or eight-reel cutter is capable of cutting as much paper in nine hours as the machine produces in twenty-four; thus, while the latter works day and night, the former need only be in action during the day.

In that made by G. & W. Bertram the paper from the several rolls passes through a pair of cast-iron drawing-in rolls, from which it is led between slitting knives on two parallel axes, similar to those already described. After passing through tube rolls, the paper is cut into lengths by means of knives set on a revolving drum, and the sheets are delivered on an apron. The length of sheet so obtained may be varied from 12 inches to the largest used by altering a change pulley, and the diameter of an expanding pulley.

Sizing.—Inferior sorts of writing paper are sized in the pulp, by the same method as printing paper; but to produce a good writing paper it is necessary to size it with animal size after it is made.

Size is generally made at the mill from the parings of skins, called *scrolls*. The gelatine can also be extracted from any of the various fibres and membranes of the animal body, and forms a considerable proportion of the bones themselves. These various materials are first soaked for several days in large wooden tubs of water, after which they are placed in a wooden cylinder from 4 to 6 feet in diameter and 10 feet in length, revolving on a horizontal shaft, which is hollow to admit of the introduction of water. The cylinder itself is perforated, and revolves in a trough, and a constant stream of water passes through it.

The cleaned clippings are now put in a tub provided with a false bottom, below which steam is introduced, but the water should never actually boil.

The method generally adopted at the present day consists in boiling these *scrolls*, *pates*, &c., in a copper for a period varying according to the nature of the membranes under treatment: care must be taken to avoid actual contact between it and the boiler, as a yellow shade would be thereby communicated to the size. The fatty matter which is extracted floats on the surface of the liquid, and must be carefully removed. After the requisite period (as much as twelve or sixteen hours in the case of ox hides, &c.), the supernatant liquid is removed and replaced by a second supply of water, and by this a weaker

solution is produced, which is usually added to the first.

The solution now requires clarifying, in order to remove the numerous substances it contains in suspension. A small quantity of powdered lime having been added, the liquid is stirred and then allowed to rest. If the impurities have not completely settled to the bottom $\frac{1}{200}$th part of sulphuric acid is added, which, forming an insoluble sulphate of lime, causes the solution to rapidly become clear, and it is then filtered through several folds of felt. In addition to gelatine, the liquid now contains chondrin, a substance which was long supposed to be identical with gelatine; and as this is a great obstacle to sizing, it becomes necessary to remove it, which can be easily accomplished by the addition of a concentrated solution of alum: sulphate of alumina or of iron would produce the desired effect. After this the size is again filtered, when it is ready for use.

The process of sizing is one of the most uncertain and difficult operations of paper making, as it is influenced in a very remarkable degree by atmospheric conditions, both of heat and moisture, and by the temperature of the size itself. If the paper is very porous it is also generally weak, and then the sizing occasions a good deal of waste. If, again, the paper has been blued with ultramarine, a strong and offensive smell is often communicated to it. The best remedy for this is to use a size which has not been long kept, to allow the paper to lie some time after being made, and after sizing to dry as quickly and as perfectly as possible. If it still retains any offensive smell this may be partially removed by hanging it up in a place where it is exposed to a very dry atmosphere.

Many attempts have been made to devise a thoroughly efficient substitute for hand sizing, but no method yet suggested can be called satisfactory. The usual system consists in drawing the paper, as delivered dry from the machine, through a properly prepared solution of size, the web being led into the liquid, contained in a flat vat, by means of suitable rolls; any superfluous size which may have been imbibed is forced out by a pair of rolls. It is then only necessary that the saturated web be dried, and this is done in the manner described below.

Hand sizing is, however, preferable for the better qualities of papers; but the practice of it requires a considerable amount of skill, and an apparatus is frequently employed, even for the sizing of hand-made papers, in which the sheets are passed between two continuous felts travelling through a solution of size, on emerging from which the superfluous size is expelled, the sheets are then slowly dried by being hung upon lines.

DRYING.—In the case of hand-made paper, the drying takes place, as just mentioned, in a well-ventilated room, the sheets being hung from lines specially made of cow hair, in order to avoid discolouring the paper.

With the introduction of the Fourdrinier machine, however, it became necessary to dry in the web; and this is accomplished by causing the web, directly on its emerging from the vat of size, to pass into a heated chamber containing the drying machine. This consists of a large iron frame supporting a number of skeleton reels, furnished with fans in their interior to agitate the air of the chamber. Over these the paper slowly passes, and it is found that the slower the drying the better is the quality of the paper. It therefore becomes necessary to largely increase the number of these skeleton reels, and chambers are frequently made containing as many as 272, over which the paper travels at the rate of about 100 feet per minute. Even this speed may be exceeded in the case of common papers.

After drying the paper is conducted through a series of rollers heated by steam, and surfaced; the final glaze being given by rolling between polished copper or zinc plates, in the manner explained below.

FINISHING.—In finishing writing paper after it comes from the cutter, it is pressed in strong hydraulic presses, and then rolled or glazed. The operation of rolling and glazing consists in subjecting the paper to a heavy pressure between highly-polished sheets of copper, zinc, or brass. This part of the work is chiefly performed by women, who take one sheet of copper and another of paper, alternately, until they have about forty of each, which is called a handful. This quantity is then passed between a pair of rollers about 14 inches diameter, set in a strong iron frame, and driven by steam or water power, working under a pressure of upwards of 20 tons. When the handful has passed through the rollers, the machinery is so constructed that its motion can be reversed, and by this means the handful is made to pass forwards and backwards several times, according to the smoothness or gloss of surface required. The construction of such a press does not call for any special notice.

CYLINDER PAPER MACHINE.—Although very seldom employed at the present day, owing to the fact that FOURDRINIER'S machine can be worked at a much more rapid speed, we should mention the existence of the process of manufacturing paper on a cylinder, the invention of Mr. DICKENSON. The apparatus consists essentially of a polished hollow brass cylinder, perforated with holes and slits and covered with wire cloth, which is caused to revolve over and in contact with the prepared pulp. The inside of the cylinder is connected with a vessel from which the air has been exhausted, and this partial vacuum causes a film of pulp to adhere to the surface of the cylinder. As this rotates the film is passed on to a second solid cylinder covered with felt, which carries it under a contiguous revolving cylinder, thus compressing the pulp, and the paper then passes over drying rolls. The machine is more especially used in the manufacture of thin tissue papers.

WATER-MARK.—Many of the curious terms employed in describing paper are derived from the very old practice of water-marking, when the different makers adopted various devices to distinguish their manufacture. Thus the terms *hand*, *pot*, *foolscap*, *post* (from a post horn), are used to designate papers of definite sizes to which they were

originally confined; the water-mark, moreover, has on several occasions been the means of detecting frauds and forgeries of various kinds; and Ireland, in his "Confessions," describes the steps he took to secure paper with the water-mark prevalent in the reign of Queen Elizabeth, for the production of his Shakspearian forgeries.

The ordinary method adopted for producing water-marks consists in affixing a stout wire of the form to be produced to the surface of the fine wire gauze of which the mould or dandy roll is constructed. This process would, however, be unavailable for the production of the finer and more intricate class of water-marks, such as those in bank notes.

Dr. Ure describes the two following processes for preparing a design for a line water-mark. In the first the design is engraved on some yielding surface, in the same manner as on a copper plate, and afterwards, by immersing the plate in a solution of sulphate of copper, and electrotyping in the usual way, all the interstices are so filled up as to give a casting of pure copper. This casting, on its removal, is ready for attaching to the wire gauze. In the second method, which is preferable when absolute uniformity is required, the design is first engraved on a steel die, the parts required to give the greatest effect being cut deepest; the die having been hardened is forced by a steam hammer into some yielding material, such as copper, and all of this metal which remains above the plane surface of the steel is subsequently removed by suitable means; the portion representing the design, being left untouched, would then be attached to the wire gauze as before. Light and shade can be communicated to the mark by a modification of the above process. For this purpose an electrotype of the raised surface of a design is first taken, and subsequently a second electrotype from this latter, which will therefore be identical with the original surface. These two are now mounted on lead or gutta percha, and employed as dies to give impression to a sheet of fine copper wire gauze, which is then employed as a mould. Absolute uniformity, such as was quite unattainable on the old system of stitching wires together, is now attained in bank notes by the adoption of the above process. It may be of interest to mention, that when the moulds were formed by stitching the fine wires together in the form of the design, no less than 1056 wires, with 67,584 twists, and involving some hundreds of thousands of stitches, were required to form a pair of five-pound note moulds, and it was obviously impossible that the designs should remain absolutely identical.

Water-proofing Papers.—M. A. Jouglet has proposed the following process for water-proofing paper, based on the solvent action on cellulose of a solution of oxide of copper in ammonia. A quantity of this solution is placed in a tank, and the paper rapidly passed just over and in contact with the surface of the liquid, by means of suitably situated rollers in motion. The paper is then pressed between a pair of rolls, and dried by the ordinary drying cylinders. The short contact of the felty substance of the paper with the liquid occasions just sufficient solution of the cellulose to form an impermeable varnish.

Transparent Paper.—Paper may be rendered transparent by being soaked in the following composition:—

Boiled and bleached linseed oil,	120 parts
Lead turnings,	6 "
Oxide of zinc,	30 "
Venice turpentine,	3 "

The mass is mixed and boiled for eight hours; after cooling it is stirred, and the following ingredients added:—

White copal,	30 parts
Sandarac,	2 "

Manufacture of Mill and Card Board.—The various kinds of boards are manufactured by one or other of the following processes:—

(1.) Superposing several leaves of paper, and uniting them by an agglutinating substance.

(2.) Superposing several wet leaves at the time of couching.

(3.) By means of moulds provided with very thick deckles. Or,

(4.) By special machines, analogous to those used for the manufacture of continuous paper.

The refuse material of all kinds existing in a paper-mill may be employed in the manufacture. The first step is sorting, when the materials are distributed according to the quality of boards for which they are suitable. After being triturated, the mass is mixed with varying proportions of rag pulp, kaolin, chalk, white clays, &c. The third method mentioned above is only adapted for boards of moderate thickness, as an excess of pulp would render the draining difficult. The processes adopted are in all respects similar to those already described in the manufacture of paper.

Micrographic and Chemical Study of Paper Fibre.—According to Girard, the principal substances used in paper-making may be divided into five classes—

1. *Round, ribbed fibres*, as hemp and flax.

2. *Smooth* or *feebly-ribbed fibres*, as Esparto, jute, phormium, dwarf palm, hop, and sugar cane.

3. *Fibro-cellular substances*, as the pulp obtained from the straw of rye and wheat, by the action of caustic lye.

4. *Flat fibres*, as cotton, and those obtained by the action of caustic lye upon wood.

5. *Imperfect substances*, as the pulp obtained from saw-dust.

He considers that the absolute length of the fibres is less important than slenderness and elasticity, and it does not appear that the fibre need possess tenacity to any special extent.

The nature of cotton, linen, and hempen rags may be determined by chemical tests, or by the microscope when the material is comparatively new.

The fibres of cotton and hemp present the appearance of rigid cylindrical tubes, with intercepted intervals, like straws, reeds, &c. They are elongated cells, glued together by a material of denser texture, which is acted on by acids and alkalies.

Hemp fibres vary from $\frac{1}{20}$th to $\frac{1}{30}$th of a millimètre in diameter; and those of linen, which have a silky appearance, are still finer. But the fibrillæ of cotton are transparent tubes, flattened in the middle throughout their entire length, and thus presenting the appearance of two parallel rolls united by a very thin partition. The diameter of these fibres vary from $\frac{1}{55}$th to $\frac{1}{85}$th of a millimètre. When the latter have been converted into textures, and these have been more or less worn, they lose their identity, and it becomes necessary to resort to chemical tests, in order to ascertain the constituents of a given substance. The two most frequently employed are:—

(1.) A boiling solution of potash colours the fibres of linen a deep yellow, whereas its action on cotton is very feeble.

(2.) Concentrated sulphuric acid rapidly attacks cotton fibres, and converts them into dextrin, while linen fibres remain white and opaque. M. VINCENT recommends the following test for distinguishing the fibres of linen and hemp from those of *Phormium tenax*:—The texture is dipped in nitric acid of 36° B. (1·33), containing hyponitric acid, when a red colour at once appears on the raw and imperfectly bleached products of the phormium, whereas the linen and hemp are very slightly, if at all, coloured.

By dipping into a saturated solution of chlorine gas, and subsequently pouring a few drops of ammonia on the sample, the threads of phormium assume a violet-red colour, which may be removed by nitric acid. Hempen threads thus treated assume a slightly rosy shade, while linen preserves its original colour.

These latter reactions can, however, only be relied upon in the case of slightly worn fibres; in practice, the sorting women can soon distinguish with sufficient accuracy by the touch.

VARIETIES OF PAPER.—It would be quite impossible to enumerate even the more important varieties of paper at present in use; it is estimated that a London wholesale stationer's warehouse never contains less than from 1000 to 2000 distinct kinds. The principal denominations of paper in the three classes, writing, printing, and wrapping, are as follows:—

- Writing:
  - Cream wove.
  - Yellow wove.
  - Blue wove.
  - Cream laid.
  - Blue laid.
- Printing:
  - Laid.
  - Wove.
- Wrapping:
  - Blue.
  - Purple.
  - Brown.
  - Whitey-brown.

The following is a list of the sizes of writing and printing paper. In a few cases there are two sizes in use, and both are given:—

	Inches.
Pott,	12½ by 15
Foolscap,	17 by 13½
Foolscap—writing,	16½ by 13¼
Post,	18¾ by 15½ or 19 by 15¼
Copy,	20 by 16
Large post,	20¾ by 16½
Medium post,	18 by 23 or 18 by 22½
Sheet-and-third foolscap,	24½ by 13¼ or 22 by 13¼
Sheet-and-half foolscap,	13½ by 25
Double foolscap—printing,	27 by 17
Double foolscap—writing,	16½ by 27
Double pott,	15 by 25
Double post,	30¼ by 19
Double crown,	20 by 30
Demy—writing,	20 by 15
Demy—printing,	17¾ by 22½
Medium,	22 by 17½
Medium—printing,	23 by 18½
Royal—writing,	24 by 19
Royal—printing,	20 by 25
Super-royal—writing,	27 by 19
Super-royal—printing,	21 by 17
Imperial,	30 by 22 or 30¼ by 22
Elephant,	28 by 23
Atlas,	34 by 26
Columbia,	34½ by 23½
Double elephant,	26¾ by 40
Antiquarian,	53 by 31

The following is a list of coarse papers, such as grey and brown:—

	Inches.
Tient cap,	21 by 18
Bag cap,	19½ by 24
Havon cap,	21 by 26
Imperial cap,	22½ by 29
Double two pounds,	17 by 24
Double four pounds,	21 by 31
Double six pounds,	19 by 28
Middle hand,	21 by 16
Lumber hand,	19½ by 22½
Royal hand,	20 by 25
Double small hand,	19 by 29

Of purples there are—

	Inches.
Copy loaf,	16¾ by 21¾
Powder loaf,	18 by 26
Double loaf,	16½ by 23
Single loaf,	21½ by 27
Lump,	23 by 33
Hambro',	16½ by 23
Titler,	29 by 35
Prussian, or double lump,	32 by 42

Statistics.—The following table is compiled from the article "Paper" in the very useful series of manuals on "British Manufacturing Industries," edited by G. P. BEVAN.

Table showing the imports and exports of paper and raw materials from 1870–75:—

YEAR.	IMPORTS.					EXPORTS.			
	Paper (Printing and Writing).		Raw Material.			Paper (Except Hangings and Papier Maché).		Raw Material.	
	Tons.	Value.	Linen and Cotton Rags in Tons.	Esparto and Vegetable Fibre in Tons.	Value.	Tons.	Value.	Tons.	Value.
1870,	8,681	£445,613	22,394	110,389	£1,202,137	8,884	£530,646	23,993	£389,909
1871,	7,864	407,480	26,757	143,313	1,680,771	11,445	668,926	33,060	588,836
1872,	10,187	578,833	22,309	104,588	1,176,435	15,254	878,592	30,546	578,019
1873,	9,767	593,552	16,151	102,751	1,128,814	15,994	973,617	16,800	297,864
1874,	9,610	509,822	17,209	119,188	1,265,276	14,088	874,114	20,215	302,332
1875,	9,401	442,871	15,879	141,319	1,384,397	16,008	941,243	24,400	326,778

The rapid increase in the Esparto trade in recent years has been already referred to (*vide ante*); but its amount now appears to have become nearly constant.

It is estimated that there are in Great Britain 350 paper mills, using 500 machines and producing about 134,000 tons annually, an amount which is nearly double the produce of twenty years ago; and the manufacture of the various qualities of paper is thus distributed in the 272 mills situated in England—

Writing papers (hand made),	21
Writing papers (machine made),	22
Printing, news and long elephant,	96
Cartridge,	29
Grocery papers (white and coloured),	48
Small hands and caps,	50
Browns,	108

The following curious information relative to the production of paper was published in Venice in 1874.

There then were 3960 paper manufacturers in the world, employing 80,000 men and 180,000 women, besides 100,000 employed in the rag trade; 1809 millions of pounds of paper were made annually, and of this half was used for printing, one-sixth for writing, and the remainder for packing, &c. In the United States 3000 machines made 200,000 tons of paper, averaging about 17 lbs. per head of the population. The average for an Englishman is 11½ lbs.; for a German, 8 lbs.; a Frenchman, 7 lbs.; an Italian, 3½ lbs.; a Spaniard, 1½ lb.; and a Russian only 1 lb. annually.

PARAFFIN. See Petroleum.

PERFUMERY.—*Parfumerie*, French; *Parfümerien*, German.—Perfumes may be divided into two groups—1, those of vegetable origin, and, 2, those of animal origin. The perfumes derived from plants may be subdivided into three classes—

Odoriferous Gums are the most ancient; they consist of the various gum-resins, which exude naturally from the trees which yield them; and to increase the yield, the trees are frequently purposely wounded. The most important are benzoin, olibanum, myrrh, and camphor.

Benzoin, also called *benjamin*, is obtained from the *Styrax benzoin*, and is imported from Borneo, Java, Sumatra, and Siam.

Olibanum, the frankincense of the ancients, is obtained from several species of *Boswellia serrata, thurifera, and glabra.*

Myrrh is obtained from the *Balsamodendron myrrha*, described by Harris as growing abundantly on the Abyssinian coast of the Red Sea. By distillation it yields an essential oil or otto; 100 lbs. of the gum yield about 8 ozs. of the otto, of which there is a sample in the Kew Museum, placed there by Dr. Piesse.

Camphor is produced by many plants. The kind mostly found in commerce is obtained from the *Laurus camphora* of the island of Formosa. The camphor exists ready formed in the plant, and is extracted by chopping the branches, and boiling them in water; the camphor rises to the surface, and becomes solid as the water cools. It is carried to Canton, from which port the markets of the world are supplied.

These odorous bodies are the chief ingredients in incense and in pastilles, and it is from the early custom of burning incense upon the altar that our word perfume, from *per fumus* (by smoke), has been derived. In this class may also be included all those parts of plants which are fragrant, such as the long seed-pod of the Vanilla plant, *Vanilla planifolia*, the finest of which comes from Mexico; the bean of the *Dipterix odorata* or tonquin bean, which our grandfathers carried in their snuff boxes, and which is still used for perfuming certain varieties of snuffs and tobaccos; the root of *Iris florentina*, or orris root; the rizome of an Indian grass known as *Vitivert*, or *Kus-kus;* fragrant woods, such as the Santal, *Santalum album*, from the Santal wood islands and the island of Timor; the myall, or violet wood of Australia; odoriferous seeds, such as the caraway, from the *Carum carui;* nutmeg and mace, both from the nutmeg tree. This class includes also the three balsams of Peru, from *Myroxylon peruiferum;* of Tolu, from *Toluiferum balsamum;* and of Storax, from *Liquidambar orientale.*

Perfumers grind these various dry odoriferous bodies to powder, and mix them in different proportions; the results are the various sachet powders.

The following are excellent recipes, and may be taken as examples:—

INCENSE.

Santal wood powder,	1 lb.
Cascarilla bark powder,	½ "
Benzoin powder,	½ "
Myrrh,	2 ozs.
Potash nitrate, powder,	2 "
Grain musk,	¼ dr.

Thoroughly mix, and sift.

Ribbon of Bruges.—This is a great improvement upon ordinary incense. Undressed tape is first steeped in a solution of potassium nitrate, and dried; then steeped in a strong tincture of gum resins. The ribbon, cut into lengths, is now coiled into vases, through a slit in the lids of which an end of the ribbon projects. On lighting the projecting end, and blowing out the flame, the ribbon smoulders, and the fragrance diffuses itself into the air. The smouldering is extinguished directly it reaches the lid of the vase.

The following is the recipe for the manufacture of ribbon of Bruges, as given by Dr. Septimus Piesse, its inventor:—

NITRE SOLUTION.

Pure nitrate of potash,	8 ozs.
Water, distilled,	1 gall.

The Tincture.

Bottle A—

Gum benzoin,	1½ lb.
" myrrh,	4 ozs.
Extract of orris,	40 " fl.

Allowed to stand for one month.

Bottle B—

Alcohol, 60° over proof,	40 ozs.
Pod musk,	2 "
Otto of roses,	½ oz.

Allowed to stand for one month.

The contents of bottles A and B are then mixed.

The tape is steeped for twelve hours in the solution of nitre, and then dried. It is then passed through the tincture, and again dried, when it is ready for use.

SACHET POWDERS.

Frangipanni Sachet.

Orris root powder,	3 lbs.
Vitivert powder,	½ lb.
Santal wood powder,	½ "
Musk pod, ground,	1 oz.
Civet,	¼ "
Otto of neroli, rose, santal, of each,	1 dr.

Lavender Sachet.

Lavender flowers, ground,	1 lb.
Benzoin powder,	½ "
Otto lavender,	1 oz.

Essential Oils.—*Distilled Perfumes.*—As soon as the Greeks and the Romans learned the use of the alembic or still, which was an invention imported by them from Egypt, they quickly adapted it to the separation of the odoriferous principle from the numerous fragrant plants indigenous to Greece and Italy. An essential oil or otto, thus procured from orange flowers, bears to this day the name of neroli, supposed to be so named from the Emperor Nero. Long before his time, however, fragrant waters were in use in Arabia.

Odour-bearing plants contain the fragrant principle in minute glands, or sacs; these are found sometimes in the rind of the fruit, as the lemon and orange; in others it is in the leaves, as sage, mint, thyme; in wood, as rose-wood and santal-wood; in the bark, as cassia and cinnamon; in seeds, as caraway and nutmeg. These bags, or glands, may be plainly seen in a thinly cut stratum of orange peel, from which the otto may be pressed out upon paper; and also in the bay leaf (*Laurus nobilis*), if it be held up to sunlight. The otto in this case is obtained chiefly from the berries.

These substances yield by distillation an otto peculiar to each. Thus, otto of patchouly, from the leaves of the patchouly plant (*Pogostemon patchouli*), a native of Burmah; otto of geranium, from the leaves of *Geranium rosa;* otto of lemon, from lemon peel (*Citrus limonum*); and a hundred others of infinite variety.

Some plants yield different varieties of oils, depending upon the part of the plant treated, and having greatly different commercial values. Thus, the orange will give three varieties—one from the rind of the fruit, called "Portugal," value in bulk about 14*s.* per lb.; one from the leaves, called "petit-grain," value £2 8*s.* per lb.; and one from the flowers, called "neroli," value about £8 per lb.

The process of distillation is very simple. The fragrant part of the plant is put into the still, and covered with water; when the water is made to boil, the ottos rise along with the steam, and are condensed with it. The distillate is received into a "separator;" the otto, floating upon the surface of the water, rises in the body of the separator, whilst the water flows from a pipe at the bottom, which pipe is bent up to nearly the level of the top of the separator; the separator is thereby kept always full, thus giving the first quantities of otto time to separate before the outflow of the water commences.

All ottos are very slightly soluble in water, so that in the process of distillation the water which comes over is always fragrant. Thus, elder water, rose water, orange water, and dill water, are, so to speak, the residues of the distillation for obtaining the ottos.

The following are examples of the quantities of ottos obtained from various sources:—100 lbs. of the fruit peel of orange, lemon, and bergamot yield about 10 ozs. of otto; 100 lbs. of cedar-wood will give about 15 ozs. of otto of cedar; 100 lbs. of nutmeg will give about 60 to 70 ozs. of otto of nutmeg; 100 lbs. of geranium leaves give about 2 ozs. otto of geranium.

The oils of lemon, bergamot, and orange, are in Italy and Sicily obtained by pressure from the rasped skins of the fruits. The ottos so obtained are much finer than those got by distillation.

The varieties of ottos are as numerous as fragrant plants; and Dr. Piesse holds that there is a certain relationship among odours, as among colours and musical sounds. The lemon-like odours are the most numerous, such as verbena (*Aloysia citriodora*), lemon, orange, bergamot, lemon-grass (*Andropogon nardus*), citron, &c.; then the almond-like odours, such as heliotrope, violet, almond, vanilla, &c.; then the spice odours, such as cloves, cinnamon, mace, cassia, &c.

Physical Properties.—The essential oils differ considerably in some of their physical properties. Many of them are perfectly colourless when pure, others are yellow, red, or brown, and a few green or blue. All have a sharp, burning, aromatic taste, and powerful odours—some agreeable, others unpleasant. They differ from fat oils in not feeling greasy to the touch, but rather make the skin brittle and rough.

As will be seen from the tables which follow, most of the essential oils are lighter than water, the specific gravities of the crude oils given lying between the limits 1·1423 and 0·8498.

We have said that a few of the oils have a green or blue colour. These are principally yielded by plants belonging to the same order as wormwood and chamomile; and Gladstone has shown that the colour is due to a deep blue compound called cœrulein, which can be obtained in more concentrated solution by repeated distillation, but which has not yet been separated in the pure form. When a solution of cœrulein in oils or alcohol is examined by means of a hollow wedge and prism, it gives a very characteristic spectrum, figured in Gladstone's original paper.

Essential oils possess great refractive and dispersive power, and exhibit peculiar effects when submitted to the action of a ray of polarized light—some being dextro, others laevo rotatory in various degrees, while a few are inactive. In the following table Gladstone gives the refractive indices for the lines A, D, and H (or G, where the yellowness of

the liquid prevented H being seen), the rotatory power, and the specific gravity of a considerable number of essential oils. The rotatory power is given for a tube 10 inches long; this length of a solution consisting of equal parts of cane sugar and water giving a rotation of 105°. It should be remarked that the product obtained by any one of the ordinary methods of preparation rarely consists of a simple volatile oil, but generally is a mixture of two or more oils. One of these—a hydrocarbon—is lighter and more volatile than the other, which is either an oil containing oxygen, or a camphor. Hence, various samples of crude oils may show slight differences in the properties here given. The history of the specimens used in the determinations (given in Table I.) was generally well known; and the examination of them gave no reason to doubt their genuineness, the only sign of impurity being a little alcohol in one or two.

It has been thought possible that some of these

TABLE I.

Crude Oils.	Specific Gravity at 15°·5 C.	Refractive Indices.				Rotation.
		Temperature.	A.	D.	H.	
Anise,	·9852	16°·5	1·5433	1·5566	1·6118	— 1°
Atherosperma moschatum,	1·0425	14°	1·5172	1·5274	1·5628	+ 7°
Bay,	·8808	18°·5	1·4944	1·5022	1·5420	— 6°
Bergamot,	·8825	22°	1·4559	1·4625	1·4779 G.	+ 23°
" Florence,	·8804	26°·5	1·4547	1·4614	1·4760 G.	+ 40°
Birch bark,	·9005	8°	1·4851	1·4921	1·5172	+ 38°
Cajeput,	·9203	25°·5	1·4561	1·4611	1·4778	0°
Calamus,	·9388	10°	1·4965	1·5031	1·5204 G.	+ 43°·5
" Hamburg,	·9410	11°	1·4843	1·4911	1·5144	+ 42° ?
Caraway,	·8845	19°	1·4601	1·4671	1·4886	+ 63°
" Hamburg, 1st dist.,	·9121	10°	1·4829	1·4903	1·5142	—
" " 2nd dist.,	·8832	10°·5	—	1·4784	—	—
Cascarilla,	·8956	10°	1·4844	1·4918	1·5158	+ 26°
Cassia,	1·0297	19°·5	1·5602	1·5748	1·6243 G.	0°
Cedar,	·9622	23°	1·4978	1·5035	1·5238	+ 3°
Cedrat,	·8584	18°	1·4671	1·4731	1·4952	+ 156°
Citron,	*·8914	—	1·4729	1·4797	1·5011 ?	—
Citronella,	·8908	21°	1·4599	1·4659	1·4866	— 4°
" Penang,	·8847	15°·5	1·4604	1·4665	1·4875	— 1°
Cloves,	1·0475	17°	1·5213	1·5312	1·5666	— 4°
Coriander,	·8775	10°	1·4592	1·4652	1·4805 G.	+ 21° ?
Cubebs,	·9414	10°	1·4953	1·5011	1·5160 G.	—
Dill,	·8922	11°·5	1·4764	1·4834	1·5072	+ 206°
Elder,	·8581	8°·5	1·4686	1·4749	1·4965	+ 14°·5
Eucalyptus amygdalina,	·8812	13°·5	1·4717	1·4788	1·5021	— 136°
" oleosa,	·9322	13°·5	1·4661	1·4718	1·4909	+ 4°
Indian geranium,	·9043	21°·5	1·4653	1·4714	1·4868 G.	— 4°
Lavender,	·8903	20°	1·4586	1·4648	1·4862	— 20°
Lemon,	·8498	16°·5	1·4667	1·4727	1·4946	+ 164°
Lemon grass,	·8932	24°	—	1·4705	—	+ 3° ?
" Penang,	·8766	13°·5	1·4756	1·4837	1·5042	0°
Lign aloes,	*·8702	—	1·4620	1·4679	—	—
Melaleuca ericifolia,	·9030	9°	1·4655	1·4712	1·4901	+ 26°
" linarifolia,	·9016	9°	1·4710	1·4772	1·4971	+ 11°
Mint,	·9342	19°	1·4767	1·4840	1·5015 G.	— 116°
"	·9105	14°·5	1·4756	1·4822	1·5037	— 13°
Myrtle,	·8911	14°	1·4623	1·4680	1·4879	+ 21°
Myrrh,	1·0189	7°·5	1·5196	1·5278	1·5472 G.	— 136°
Neroli,	·8789	18°	1·4614	1·4676	1·4835 G.	+ 15°
"	·8743	10°	1·4673	1·4741	1·4831 F.	+ 28°
Nutmeg,	·8826	24°	1·4644	1·4709	1·4934	+ 44°
" Penang,	·9069	16°	1·4749	1·4818	1·5053	+ 9°
Orange-peel,	·8509	20°	1·4634	1·4699	1·4916	+ 32° ?
" Florence,	·8864	20°	1·4707	1·4774	1·4980	+ 216°
Parsley,	·9926	8°·5	1·5068	1·5162	1·5417 G.	— 9°
Patchouli,	·9554	21°	1·4990	1·5050	1·5194 G.	—
" Penang,	·9592	21°	1·4980	1·5040	1·5183 G.	— 120°
" French,	1·0119	14°	1·5074	1·5132	1·5202 F.	—
Peppermint,	·9028	14°·5	1·4612	1·4670	1·4854	— 72°
" Florence,	·9116	14°	1·4628	1·4682	1·4867	— 44°
Petit grain,	·8765	21°	1·4536	1·4600	1·4808	+ 26°
Pimento,	*1·0374	—	1·5229	1·5325	1·5660 ?	—
Rose,	·8912	25°	1·4567	1·4627	1·4835	— 7°
Rosemary,	·9080	16°·5	1·4632	1·4688	1·4867	+ 17°
Rosewood,	·9064	17°	1·4843	1·4903	1·5113	— 16°
Santalwood,	·9750	24°	1·4959	1·5021	1·5227	— 50°
Thyme,	·8843	19°	1·4695	1·4754	1·4909 G.	—
Turpentine,	·8727	13°	1·4672	1·4732	1·4938	— 79°
Verbena,	·8812	20°	1·4791	1·4870	1·5059 G.	— 6°
Vitivert,	*1·0070	—	1·5147	1·5218	—	—
Wintergreen,	1·1423	15°	1·5163	1·5278	1·5737	+ 3°
Wormwood,	·9122	18°	1·4631	1·4688	1·4756 F.	—

* The specific gravity and refraction of citron, lign aloes, pimento, and vitivert is given for the temperatures 10°, 18°, 10°, and 19°·5 respectively.

physical characters may be of service in detecting the fraudulent admixture of oils. The addition of oil of turpentine would, in almost every instance, have the effect of lowering the specific gravity and contracting the spectrum. Again, pure oil of bergamot has a low refraction, lower doubtless than those mixtures which are often sold under its name.

Most of the essential oils existing ready formed in plants contain hydrocarbons of the formula $nC_{10}H_{16}$. In some cases they are accompanied by a viscid resin, which is a product of the oxidation of the hydrocarbons, while in others the relation between the two constituents of the oil is not apparent. In the following table will be found some of the properties of the hydrocarbons, prepared from the crude oils by fractional distillation and frequent rectification over sodium. They are arranged according to their specific gravities at 20° C. The column headed "Dispersion at 20° C." gives the difference between the refractive indices of the lines H and A. The sensitiveness is the amount of diminution of the refractive index when the temperature rises 10° C.; it is calculated for the line A, and the number 48 is a short expression for 0·0048. The specific refractive energy is the refractive index, minus unity, divided by the density. In the annexed Table II. it is taken for A; that is to say, if μ stand for the refractive index, the column represents $\frac{\mu_A - 1.}{D}$

It will be seen that these hydrocarbons divide themselves into two great groups, the line of separation being between those from rosemary and cloves. The first group, with a lower specific gravity, has always a far lower boiling point, a smaller index of refraction, and a higher sensitiveness.

And these large groups are capable of subdivision. The first ten hydrocarbons in the table resemble one another very closely, and it is not unlikely that some of them are identical rather than isomeric. The hydrocarbons from wormwood, anise, thyme, mint, and laurel turpentine group with ordinary turpentine bay, myrtle, and rosemary stand alone, each having a low refraction and dispersion, but they differ much in specific gravity.

In the second large group the hydrocarbons from cloves and rosewood appear nearly, if not quite, identical in properties, and are certainly different from patchouli, calamus, and cascarilla. Colophene differs from the second large group in much the same way as that differs from the first, though to a smaller extent.

The groups thus distinguished are represented by

TABLE II.

Source of Hydrocarbon.	Specific Gravity at 20° C.	Boiling Point.	Refractive Index, A at 20° C.	Dispersion at 20° C.	Sensitiveness.	Specific Refractive Energy.	Rotation.
		Degrees C.					
Orange peel,	·8460	174	1·4645	·0277	48	·5490	+ 154
" Florence,	·8468	174	1·4650	·0281	49	·5491	+ 260
Cedrat,	·8466	173	1·4650	·0280	49	·5492	+ 180
Lemon,	·8468	173	1·4660	·0280	49	·5502	+ 172
Bergamot,	·8466	175	1·4619	·0295	49	·5456	+ 76
" Florence,	·8464	176	1·4602	·0287	48	·5437	+ 82
Neroli,	·8466	173	1·4614	·0291	47	·5450	+ 76
Petit grain,	·8470	174	1·4617	·0282	46	·5439	+ 60
Caraway, Hamburg, 1st dist.,	·8466	176	1·4645	·0286	48	·5486	+ 180
Dill,	·8467	173	1·4646	·0288	46	·5486	+ 242
Cascarilla,	·8467	172	1·4652	·0305	49	·5494	0
Elder,	·8468	172	1·4631	·0269	47	·5468	+ 15
Bay	·8508	171	1·4542	·0260	47	·5338	— 22
Gaultherilene,	·8510	168	1·4614	·0271	49	·5422	—
Nutmeg,	·8518	167	1·4630	·0284	47	·5435	+ 49
" Penang,	·8527	166	1·4634	·0274	49	·5434	+ 4
Carvene,	·8530	166	1·4610	·0261	48	·5440	— 20
" Hamburg, 2nd dist.,	·8545	—	1·4641	·0263	48	·5431	+ 86
Wormwood,	·8565	160	1·4590	·0253	47	·5359	+ 46
Terebene,	·8583	160	1·4670	·0275	48	·5440	0
Anise,	·8580	160	1·4607	·0268	47	·5368	—
Mint,	·8600	160	1·4622	·0255	48	·5374	+ 30
Peppermint,	·8602	175	1·4577	·0267	47	·5321	— 60
Laurel peppermint,	·8618	160	1·4637	·0260	47	·5380	+ 94
Thyme,	·8635	160	1·4617	·0282	48	·5346	— 75
Turpentine I.,	·8644	160	1·4612	·0250	47	·5335	+ 48
" II.,	·8555	160	1·4590	·0256	47	·5365	— 87
" III.,	·8614	160	1·4621	·0249	—	·5364	— 90
" IV.	·8600	160	1·4613	·0254	47	·5364	— 88
Eucalyptus amygdalina,	·8642	171	1·4696	·0323	49	·5434	— 142
Myrtle,	·8690	163	1·4565	·0248	47	·5253	+ 64
Parsley,	·8732	160	1·4665	·0291	46	·5355	— 44
Rosemary,	·8805	163	1·4583	·0241	46	·5205	+ 8
Cloves,	·9041	249	1·4898	·0284	45	·5417	—
Rosewood,	·9042	249	1·4878	·0277	45	·5395	— 11
Cubebs,	·9062	260	1·4950	·0302	41	·5462	+ 59
Calamus,	·9180	260	1·4930	·0322	42	·5370	+ 55
" Hamburg,	·9275	260	1·4976	·0337	43	·5365	+ 22
Cascarilla,	·9212	254	1·4926	·0307	42	·5347	+ 72
Patchouli,	·9211	254	1·4966	·0274	42	·5391	—
" Penang,	·9278	257	1·4963	·0275	44	·5349	— 90
" French,	·9255	260	1·5009	·0262	42	·5412	—
Colophene,	·9391	315	1·5084	·0309	41	·5413	0

formulæ in which the number of carbon atoms is different, though the ratio between carbon and hydrogen remains the same, and Gladstone has summed up in the appended Table III. the differences in physical properties exhibited by them. It is probable that paracajputene, as well as other substances, are isomerides of colophene.

There is no difference in specific refractive energy. The various members of the 10 and 15 carbon groups have powerful odours, and rotate the plane of polarization strongly, sometimes in one, sometimes in the other direction.

Of the physical properties of the oxidised constituents of essential oils not so much is known, Table IV. embraces most of the determinations made by Gladstone:—

TABLE III.

	10-Carbon Group.	15-Carbon Group.	20-Carbon Group.
Formula,	$C_{10}H_{16}$	$C_{15}H_{24}$	$C_{20}H_{32}$
Vapour density,	4·7	7·1	—
Character of liquid,	Limpid.	Viscid.	Very viscid.
Specific gravity at 20° C.,	0·846—0·880	0·904—0·927	0·939
Refractive index for A at 20° C.,	1·457—1·467	1·488—1·497	1·5084
Dispersion,	About 0·027	About 0·029	0·031
Sensitiveness,	About 48	About 43	41
Boiling point,	160°—176°	249°—260°	315°
Action of sulphuric acid,	Polymerizes.	Doubtful.	None.
Solubility in aqueous alcohol,	Freely soluble.	Sparingly soluble.	Insoluble.
Combination with HCl,	$C_{10}H_{16}.2HCl$ and $C_{10}H_{16}.HCl$	$C_{15}H_{24}.2HCl$ and in smaller proportions.	Very small quantity.

TABLE IV.

	Specific Gravity at 20° C.	Boiling Point.	Refractive Index A at 20° C.	Dispersion at 20° C.	Sensitiveness.	Rotation.
Citronellol, Penang,	0·8742	200°	1·4563	0·0251	50	—
" Ceylon,	0·875	200°	1·4594	0·0262	46	— 13
Absinthol,	0·9267	217°	1·4543	0·0243	43	+ 134
Cajeput,	0·9160	174°	1·4532	0·0213	45	— 2?
Melaleuca ericifolia,	0·8960	173°	1·4560	0·0239	48	+ 30
" linarifolia,	0·8985	173°	1·4651	0·0263	46	+ 11
Eucalyptus oleosa,	0·9075	171°—176°	1·4563	0·0227	44	+ 10
Carvol,	0·9530	227°	1·4886	0·0345	46	+ 145
Dill carvol,	0·9562	—	1·4891	0·0333	45	+ 108
Menthol I.,	0·9515	225°	1·4839	0·0326	44	— 103
" II.,	0·9394	225°	1·4791	0·0311	42	— 114
Myristicol,	0·9466	224°	1·4848	0·0312	46	+ 31
Rose,	0·881	216°	1·4647	0·0283	47	—
Indian geranium,	0·884	—	1·4692	0·0295	59	— 3
Atherosperma moschatum,	1·0386	224°	1·5143	0·0460	46	+ 10
Lign aloes,	0·8640	200°	1·4601	0·0280	—	—

Menthol and myristicol are the oxidised oils from mint and nutmeg respectively.

All essential oils are soluble in alcohol, fat, and fixed oils, the principal consumption of them being for scenting soap, and the manufacture of simple essences by dissolving them in alcohol. The following are examples of simple essences:—

ESSENCE OF LAVENDER.

Otto of lavender (English), ... 6 ozs.
Alcohol, 60° over proof, ... 1 gallon.

ESPRIT DE ROSE.

Otto of roses, ... 3 ozs.
Alcohol, 60° over proof, ... 1 gallon.

Scented Soaps.—For scenting of soaps the perfumer starts with fine soaps in the raw state, purchased from the soapmaker. These are "remelted," perfumed, and coloured according to the product required, in the following way:—

The bar soap is cut up into thin slabs by pressing the bars against a fine piano wire, made taut between two screws on the working bench. These screws regulate the height of the wire from the bench, and hence the thickness of the slabs cut from the bars. The melting pans are iron vessels made of various sizes, capable of holding from 28 lbs. to 3 cwts., and are heated by a steam jacket, or water bath. The soap is put into the pan in "rounds," that is, the thin slabs of soap are placed perpendicularly all round the sides of the pan; a few ounces of water are introduced, the steam of which assists the melting. The pan is then covered, and in about thirty minutes the soap will have "run down;" another "round" is then put in and melted; this is repeated every half hour until the "melting" is completed. When different soaps are being remelted together to form one kind when finished, the various sorts must be put into the pan in alternate rounds, each round consisting entirely of only one variety, to insure uniformity of condition. As the soap melts it is stirred from time to time with a "crutch." The form of this instrument is indicated by its name; it is like an inverted ⊥, a long wooden handle with an iron cross-plate carved to fit the pan; the colouring matter and the perfume are added when the soap is quite melted; and when well crutched in

the soap is turned into a "frame;" the frame is a box made in horizontal sections, so that it can be taken to pieces, in order that the soap may be cut up when cold, which will be in about thirty-six to forty-eight hours.

The following recipe is an example of a remelted perfumed soap, known as—

ALMOND SOAP.

Finest curd soap,	1	cwt.
" oil soap,	14	lbs.
" marine soap,	14	"
Otto of almonds,	1½	"
" cloves,	¼	"
" caraway,	½	"

Melt half of the curd soap, then add the marine soap; well crutch this, then put in the oil soap, and finish with the remainder of the curd. When the whole is quite melted crutch in the mixed ottos, and turn into the frame.

For the production of very highly scented soaps, with ottos of an expensive character, the process of scenting them *cold* is employed. This is a far more convenient method for small quantities, and much more economical, since it prevents the loss by evaporation of the ottos, which occurs to the extent of about 20 per cent. of the ottos used in the hot process.

The cold process is conducted as follows:—About 14 lbs. of the bars of the finest curd, or other soap, previously remelted and coloured to the required tint, are reduced to shavings by being pushed across a plane temporarily fixed over a large marble mortar; the requisite quantity of perfume is then added, and the whole incorporated with a *lignum vitæ* pestle until it is of one uniform consistence; it is then weighed in quantities of the proper weight for the size of the tablets required. These masses are roughly moulded into egg-shaped forms by hand, and allowed to dry for about forty-eight hours, after which they are struck in a press. The following are the substances used to colour soaps:—

Rose.—Curd soap stained with rosaniline.

Blue.—Curd soap coloured with smalt ground in water.

Green.—Palm oil soap and smalt ground in water.

Mauve.—Curd soap coloured with aniline mauve.

Brown.—Curd soap coloured with caramel.

Some soaps become sufficiently coloured by the incorporation of the ottos used to perfume them, such as "spermaceti" soap and "lemon" soap.

The following recipes will serve as examples of "cold" scented soaps:—

OTTO OF ROSE SOAP.

Curd soap, previously tinted pink,	4½	lbs.
Otto of rose,	1	oz.
" santal,	½	oz.
" geranium,	¼	oz.
Essence of musk,	2	ozs.

Mix the perfumes, stir them into the soap shavings, and beat together. Retail value about 10*s.* per lb.

TONQUIN MUSK SOAP.

Curd soap, tinted light brown,	5	lbs.
Grain musk,	½	oz.
Otto of bergamot,	1	"

Rub the musk with the bergamot, and then add it to the soap, and beat up. This requires to be at least six months old before being used.

Dentifrices, &c.—

VIOLET POWDER—FOR INFANTS.

Wheat starch,	12	lbs.
Orris root powder,	2	"
Otto of lemon,	½	oz.
" bergamot,	¼	"
" cloves,	2	drs.

Well rubbed together; then sifted through a fine sieve.

PISTACHIO-NUT TOILET POWDER.

Starch of pistachio nuts,	7	lbs.
French chalk (steatite in fine powder),	7	"
Otto rose and lavender, each,	1	dr.

Same manipulation as above.

TOOTH POWDERS (DENTIFRICES)—CAMPHORATED CHALK.

Precipitated chalk,	1	lb.
Orris-root powder,	½	"
Powdered camphor,	¼	"

Reduce the camphor to powder by rubbing it in a mortar with a little alcohol; then sift the whole well together.

FARINA PIESSE'S COLOGNE DENTIFRICE.

Burnt horn,	2	lbs.
Orris-root powder,	2	"
Carmine,	1	dr.
Very fine powdered loaf sugar,	½	lb.
Ottos of lemon, bergamot, and petit grain d'orange (orange peel), each,	½	oz.
Otto of neroli,	½	dr.
" rosemary,	1	"

Thoroughly well mix, then sift.

Flower Perfumes.—These are the perfumes proper. It will have been observed that hitherto no reference has been made to the fragrance from *flowers*, but only those odours which are derived from either the leaves, seeds, wood, fruits, or roots of plants.

Nearly all the perfumes derived from flowers are made by the processes known as *enfleurage*, or inflowering, and maceration, or infusion.

Enfleurage.—The exhalation from the flowers is very rapidly absorbed by animal fats or by oils, and upon this fact is founded the process, which is thus conducted:—

Lard, or beef-suet, thoroughly purified by melting, washing, &c., is spread upon each side of a *chasse-en-verre* to the thickness of about half an inch. The *chasse-en-verre* is a frame with a glass pane in it, as near as possible like a window sash, except that the frame is 2 inches thicker, so that when one chasse is placed upon another there is a space of 4 inches between the glasses. These frames are about 3 feet long and 2 feet wide; there are generally about 3000 of them in a flower laboratory. When the grease is spread upon each side of the glass of each chasse, it is sprinkled with fresh blossoms, the chassis being piled one upon another, so that the flowers are inclosed, having the grease above and below them; the blossoms are changed every day, or every alternate day, as regulated by the

flowering of the plants. The same grease, however, remains in the chassis so long as the particular plant being used yields blossoms. Each time that fresh blossoms are put on, the grease is "worked," that is, serrated with a spatula or a wooden fork, so as to expose a fresh surface. The grease being thus inflowered for three weeks or more, is at last scraped off the chassis, melted, strained, and poured into tin canisters, and is now fit for exportation.

For the *enfleurage* of oil, a *chasse-en-fer* is used; the place of the glass being occupied by a wire net, on which is laid a *molleton*, or thick cotton fabric soaked in olive oil; on this the blossoms are laid just as upon solid grease.

In due time the oil becomes fragrant, and it is then pressed out of the fabric in a screw-press.

Maceration is infusion of the flowers in oil or melted fat. For this end purified fat is melted in a *bain-marie*, or water-bath. If the grease is just fluid it is sufficiently hot. The blossoms are infused for several hours, then the spent blossoms are strained away, and fresh flowers added so long as they can be procured. Although oil does not require to be heated, improved results are obtained when it is slightly warmed. Tuberose and jasmine produce perfumed grease best by enfleurage; rose, orange, and acacia give best products by maceration; while violet and jonquil grease is best obtained by the joint processes—enfleurage followed by maceration.

In order to obtain the perfume of these flowers in the form used for scenting the handkerchief, the scented fat or oil, obtained by either of the methods described above, is infused in strong alcohol of 60° over proof. In extracting the odour from solid fats, they have to be chopped up fine, and then put into the spirit, and left to infuse for about a month; in the case of oils they have to be intermittently agitated with the spirit during the whole of the month. The result is that the spirit extracts all the odour from the fatty body, becoming itself perfumed, while the fat, or oil, becomes again odourless. Essence of jasmine, essence of violets, &c., are procured in this way.

It is a remarkable fact that the essences of the flowers named above yield perfumes, which, either separate or mixed in various proportions, are the types of nearly all flower odours. Thus, when jasmine and orange flowers are blended, the perfume produced is that of the sweet pea; when jasmine and tuberose are mixed, the resulting odour is that of the hyacinth. All the various bouquets, exemplified in the following recipes, are made upon this principle:—

SWEET BRIER, OR EGLANTINE.

Alcoholic extract of rose pomatum,	1 pint.
" cassie pomatum,	½ "
" fleur d'oranger,	½ "
Esprit de rose,	¼ "
Otto of neroli,	½ dr.
Otto of lemon grass,	½ "

The whole to be mixed; it is then fit for use.

FRANGIPANNI—THE ETERNAL PERFUME.

Recipe to make 10 gallons.

Alcohol, 60° over proof,	8¾ galls.
† Extract of orris,	1⅝ gall.
* Tonquin beans, chopped,	1¼ lb.
* Pod musk,	2 ozs.
* Vanilla beans, cut fine,	10 "
* Ambergris,	½ oz.
Alcoholic extract of cassie, tuberose, fleur d' oranger, and rose pomatums, each	1½ pint.
Otto of rose and cedar, each	4 ozs.
" geranium,	1½ oz.
" neroli,	2 ozs.
" Portugal,	½ oz.

Not to be used till about two months old.

RONDELETIA.

Alcohol, 60° over proof,	1 gall.
Otto of lavender,	2 ozs.
" cloves,	1 oz.
" roses,	3 drs.
" bergamot,	1 oz.
Alcoholic extract of musk, vanilla, and ambergris, each	¼ pint.

The mixture to be at least one month old before being used.

Flower Farming.—*Roses.*—In the valley of the Var the field is first scantily manured; it is then ploughed, with oxen at the yoke. Young plants of roses, procured from layers in the usual way, by tongueing and laying at a joint, or the offshoots from the mother plant, are planted in rows, 2 feet from each other, the rows being 5 feet apart. Each root before being planted should be cut down to within two or three buds. The Cabbage Provence Rose is the kind cultivated. It is not until the fourth year that they are fully developed, although a considerable quantity of flowers appear in the second year. A plantation of roses, if well tended, will last from seven to eight years. About 7000 rose plants are required to cover an acre; and this acre will produce in an average season about 5000 lbs. weight of blossoms, of the value of about five farthings per pound, yielding therefore about £30 per acre.

Cassie.—The young plants are raised from seed, sown in beds. All doubtful plants are removed, leaving only the most vigorous. In the third year they have generally a height of between 2 and 3 feet; they are then planted out in fields, each plant requiring 12 square feet. A situation well exposed to the sun should be well dressed with manure, and dug to the depth of 4 to 6 feet, in which to plant the young cassie trees.

The blossoms of cassie are successive; that is, some are ready for plucking while others are scarcely formed. This is of immense advantage to the farmer, as it enables him to gather, and pass through the laboratory, one lot of blossoms before the others are ready for plucking. After the third year the tree produces flowers, growing, at the same time, till it reaches maturity, when it attains a height of

* The substances to which an asterisk is prefixed are to be placed together in a thin muslin bag, and suspended in the spirit for one month.

† Extract of orris is thus made:—7 lbs. of broken dried orris root are infused in 1 gall. of spirit for one month.

10 to 12 feet, with a stem 3 or 4 inches in diameter, and throwing branches 6 feet in length. Each full-grown tree will produce annually about 2 lbs. weight of flowers, value about 3½*d.* per lb., say £35 per acre. Flowers are not of much use, practically, in the perfumer's laboratory unless they grow "successive," because if they come all together there is not sufficient time for the grease to be inflowered; it is found that better results are obtained by "repeating" a small quantity of flowers over grease, than inflowering a large quantity of blossoms at one time.

Jasmine is cultivated by slips of the wild jasmine grafted at the end of two years with the Spanish jasmine. This produces a blossom the size of a shilling, and of intense fragrance. Jasmine requires a moist soil, or to be so situated that it can be freely irrigated. The distance of planting out the jasmine is the same as for the rose; it must be liberally pruned each year. The flowers of the jasmine are produced from July to the end of October, but those of August and September are the most fragrant. About fifty consecutive daily inflowerings produce the finest jasmine fat. It requires about 8000 plants to stock an acre. They are planted in rows, horizontal poles being thrust between them for support, the branches being woven in and out, somewhat as the raspberry canes are arranged in this country. The plants are not in full bearing until the second year after grafting; but when mature, every thousand plants yield about 60 lbs. weight of flowers each year. An acre of land will yield about 500 lbs. weight of jasmine blossoms of the value, on an average, of 1*s.* 3*d.* per pound.

Tuberose.—This is a bulbous plant. It throws out a stem covered at the extremity with fleshy flowers like those of a hyacinth. It is the most difficult plant on the farm to rear, and the best worth rearing. It requires to be planted in a moist soil, or where it can be freely irrigated. About 6 lbs. weight of the flowers are required to perfume 2 lbs. of grease; the value of the blossoms being about 2*s.* per pound.

Orange.—This tree is raised from seeds or pips; at the third year they are grafted either with the sweet Portugal or the bitter Bigaradier; at the fifth year they are transferred to their permanent resting-place. Before planting the orange the soil on which it is to live must be well prepared; it must be trenched at least 4 feet deep, and well manured. The care bestowed upon the young plants will be seen fifty, and even a hundred years afterwards. There are several plantations of orange trees at Nice more than a century old, and at Fontainebleau orange trees are still to be seen planted by an ancestor of the writer two hundred years ago. The tree requires about fifteen years to come to maturity, but will produce both flowers and fruit in four or five years. When in full vigour each tree yields an average of 25 lbs. weight of blossoms annually. There is at Nice, during the season, a public market for orange blossoms. The bitter orange flowers fetch about 3*d.* per lb., and the sweet 2*d.* During the season, which on an average lasts a month, there are sold about 15 to 18 tons of flowers daily. One ton of flowers will yield by distillation about 40 ozs. of the otto (neroli), which is computed to be worth £20, and the residuary water, saturated with odour, worth about £10.

Violet.—This plant must be shaded from the sun. It is propagated by division of the roots, which are planted so as to grow in clusters, about a foot apart all round. After the young plants are set out and well rooted they must have a dressing of liquid manure, which should be repeated every year about two months before they come into flower. The old plants should be removed about every sixth year, and be replaced by young ones. An area of land equal to an acre of plants will yield about 180 lbs. to 200 lbs. of flowers, annually valued at about 1*s.* 8*d.* per lb. The kind grown is the "double Parma." The violet blossom harvest amounts to about 25 tons annually at Nice.

Geranium.—The rose leaf or oak leaf geranium is grown for the sake of the rose-like otto extracted by distillation from the leaves, a ton of which will yield about 2 lbs. of the otto. It is largely used to adulterate otto of roses; it is in its turn also adulterated with ginger-grass oil (*andropogon*). The value of the last is about 6*s.* per lb., while the genuine geranium leaf otto is worth about 5*s.* per ounce. The plant is propagated by cuttings made in September, and put out in the spring; the land should be pretty well dressed with manure, and, if the season is dry, the plants well watered. They grow to a height of 3 to 4 feet, yielding an abundance of foliage, which is easily gathered by the sickle.

Lavender of the finest quality is grown in England; farms of it exist at Mitcham in Surrey, at Hitchin in Hertfordshire, and at Market Deeping in Lincolnshire. About 3500 plants are required to stock an acre, which yield when in full bearing about 6 or 7 quarts of otto of the value of about £2 14*s.* per lb. weight: say averaging about £32 per acre. The plants are propagated from cuttings, and require to be renewed about every third year.

Rosemary, *Thyme*, and *Lavender* are grown to a vast extent in the high regions of the maritime Alps. They can scarcely be said to be "cultivated" singly, they grow like the heaths on the wolds of Yorkshire. The persons who seek the ottos of these plants carry the distilling apparatus up the hills on the backs of mules, and encamp themselves in tents near to some snow stream.

Animal Perfumes.—These are four only in number, viz.:—1, Musk; 2, civet; 3, castor; 4, ambergris.

Musk is a peculiar substance secreted in excretory follicles about the navel of the male musk deer (*Moschus moschatus*). This animal is an inhabitant of the great mountain range which belts the north of India, and branches out into Siberia Thibet, and China, and of the Altaic range near Lake Baikal, living always on the borders of the line of perpetual snow. In the perfumery trade the little bags containing the musk are called "pods"; as imported it is known as "pod musk." When the musk is

removed from the skin containing it, it is called "grain musk." The musk deer is rather more than 3 feet long, and about 2 feet high at the shoulder. The head is small, the ears long and erect. The male has a tusk depending from each side of the upper jaw, which in the full grown animal is about 3 inches long, the thickness of a goose quill, sharp pointed, and curved slightly backwards. The general colour is a dark speckled brownish-grey, deepening to nearly black on the hind quarters. The legs are long and slender; the toes (of the cloven hoofs) long and pointed. The fur is composed of thick, spiral hairs, not unlike miniature porcupine quills. The tail, which is not seen unless the fur is parted, is about an inch long, and of the thickness of a thumb; in the female and young it is covered with hair; but in the adult male it is bare, with the exception of a slight tuft at the end.

The "pod" is placed near the navel, between the flesh and the skin, and is composed of several layers of thin skin in which the musk is confined. There is an orifice outwards through the skin into which the little finger will pass, but it has no connection whatever with the body. It seems probable that musk is at times discharged through this orifice, as the pod is frequently found not half full, and sometimes nearly void. A weak alkali, such as soap, is favourable to the development of the odour of musk; but if a powerful alkali, such as a strong solution of caustic potash, be poured on to grain musk, ammonia is evolved, and the true smell of musk lost. The odour of musk is quickly discharged by a solution of potassium cyanide.

There are three qualities of musk known in the London market, viz.:—

Cabardien or *Russian Musk.*—Rarely, if ever, adulterated; poor in fragrance; value about 8*s.* per ounce in pod.

Assam Musk.—Very strong, but with a rank smell; pods large, and of irregular shape; value about 24*s.* per ounce in pod.

Tonquin or *Chinese Musk* is the finest kind; more frequently adulterated than No. 2; value about 28*s.* to 38*s.* per ounce in pod.

The following two "extracts" of musk are made:—

EXTRACT OF MUSK.

Grain musk,	2 ozs.
Alcohol, 60° over proof,	1 gallon.

Infuse for one month before using.

EXTRAIT DE MUSC.

So called.

Extract of musk (No. 1) above,	1	pint.
" ambergris,	½	"
" rose triple,	¼	"

Mix; and, if necessary, filter. Fit for use at once.

Civet.—This is the peculiar secretion of the civet cat (*Viverra civetta*). It is formed in a large double glandular receptacle between the anus and pudendum of the animal. The Dutch used to keep a large number of civets alive for the purpose of collecting the perfume when secreted. The collection took place about twice a week by placing the animal into a long wooden cage, so narrow that the animal could not turn itself round; the cage being opened by a door behind, a small spatula or spoon was introduced through the orifice of the pouch, which was carefully scraped, and the contents placed into a vessel. The yield was about a drachm each time, the quantity being influenced by the quality of the food supplied, and the quantity which the animal ate. Its favourite food was boiled meat, eggs, birds, and small animals, and particularly fish. There is a living specimen of the animal in the gardens of the Zoological Society, Regent's Park. The civet now brought to European markets comes chiefly from Calicut, Bassora, and from Abyssinia.

Extract of Civet is prepared by rubbing in a mortar 1 oz. of civet with 1 oz. of orris root powder, or any other material that will divide the civet, and placing the whole into 1 gallon of alcohol, of 60° over proof. After infusion for one month, the perfume is fit for use: 4 to 8 fluid ozs. is the utmost of this extract that should be mixed with a gallon of any other perfume.

Castor is a secretion of the *Castor fiber*, or Beaver. It is imported from Canada and the Hudson Bay Territory. The substance is contained in small pear-shaped membranous sacs or pouches, hard and brittle in this country, but asserted to be soft and pasty, like civet, when taken from the animal. When dry, the castor has but little odour; but when infused in alcohol, the perfume is developed to a remarkable degree. Two ounces of castor, infused for one month in a gallon of alcohol of 60° over proof, is the standard extract. Not more than about 4 to 6 ozs. of this extract should be mixed with a gallon of any other perfume, or its characteristic odour becomes evident above all the others.

Ambergris.—This substance is found floating in the sea, near the islands of Sumatra, Molucca, and Madagascar; also on the coasts of America, Brazil, China, Japan, and the Coromandel. Large pieces of it are often found on the western coast of Ireland. For a long time it was supposed to be the fœces of the spermaceti whale (*Physeter macrocephalus*), because good specimens of it were found to contain the horny beak of cuttle-fish, upon which the whale is known to feed. It appears certain now, however, that the ambergris is a sort of intestinal calculus thrown up by the spermaceti whale; its characteristics appertain both of the nature of biliary calculus and of excrement. It appears to acquire its peculiar fragrance from oxidation by contact with air.

It is used to give permanence to the more volatile and fleeting essences for the handkerchief, and is much valued by the perfumer for this purpose, who uses it in the form of—

EXTRACT OF AMBERGRIS.

Alcohol 60° over proof,	1 gallon
Ambergris,	3 ozs.

Allowed to stand, with occasional stirring, for one month.

When sold to the consumer it has to be "sweetened," and it is then called—

EXTRAIT D'AMBRE.

Extract of ambergris,	1 pint
" vanilla	2 ozs.
Esprit de rose, triple,	½ pint
Extract of musk,	¼ pint.

The mixture is fit for immediate use.

PETROLEUM, *πετρα*, a rock, and *oleum*, or possibly *ἔλαιον* oil.—*Pêtrole*, French; *Steinöl*, German.—Rock oil is a name applied to the several bituminous fluids which are found in many parts of the earth, saturating the soil, exuding from it, or rising from its surface as oil springs. These fluids differ greatly from one another in physical characters—colour, consistency, odour, &c., though chemically they are closely allied (see also BITUMEN).

Class Characteristics.—Before going more particularly into the characters, &c., of this class, it will be advisable to take a general view of the whole field of bituminous substances, and observe the more prominent relationships existing between the various members of the class of substances frequently collectively termed bitumen.

Bitumens are found of all degrees of consistency, and of varying shades of colour; from the clear limpid naphtha of Georgia, on the Caspian, to the great "bitumen lake" of Trinidad. Though they differ thus physically, in chemical composition they are all either hydrocarbons or the products of the oxidation of hydrocarbons, the lighter and clearer consisting wholly of carbon and hydrogen; whilst the heavier, darker, more solid varieties, usually contain oxygen as a constituent, together with these elements. They are still more intimately related in chemical composition than this fact would indicate; for out of the numerous series into which the great family of hydrocarbons has been divided, it is found that the various bituminous products consist almost entirely of the members of two of these series, viz.—the marsh gas and the olefiant gas or ethylene series.

The different members of which these series are composed differ from one another in some important particulars.

The lowest members are gaseous at ordinary temperatures, as their names, which are used in designating the series, would indicate. Next in order we have very light liquids, with a comparatively low boiling point, and which will be seen by the table given further on to have a higher formula—*i.e.*, more atoms in the molecule than those preceding them. From these, the molecules still increasing by successive additions of one or more increments of CH_2, we pass through a number of liquids, which, as their formulæ become higher, steadily increase in boiling point and specific gravity till we reach the highest members, those consisting of 20 or more carbon atoms in the molecule, which are the substances, solid at ordinary temperatures, known as paraffin.

The lightest of these liquid bitumens is known as native naphtha. It is found in its purest form at Baku, in Georgia, on the western shore of the Caspian Sea. In the centre of the tract of country which yields oil, the product is as clear and pure as if distilled, and its faint yellow tint has been compared to that of Sauterne wine.

The term naphtha is also frequently applied to the lighter portions distilled from heavier oils, from peat, bituminous shales, and other oil-yielding sources, and must not be understood to mean this, unless qualified by some word indicating its origin.

The specific gravity of native naphtha varies between ·700 and ·850. In it, as might be expected, only the lower members of the marsh gas series will be found; the first—marsh gas itself—constantly escaping by innumerable jets from the vicinity of the spring, sometimes in such quantity as to form a stream of inflammable gas.

We next come to the various qualities of crude oil, correctly designated petroleum. Those from different regions of the earth, and even those from different springs in the same district, vary considerably. In some cases they are very highly coloured—though the essential constituents of petroleum are quite devoid of colour—yellow, reddish brown, greenish, and black are found; and the depth of colour, in conjunction with the odour is usually an indication of the amount of impurity present, which may be bitumenized organic matter, sulphur compounds, carbon, &c. The density, too, varies a good deal, the purer kinds having a lower specific gravity and yielding a larger proportion of light oil by distillation; whilst the more highly coloured, heavier varieties, contain chiefly higher members of the two series of carbon compounds. The usual range of specific gravity of petroleum may be taken at from ·782 to ·820 (CHANDLER, *Amer. Chem.* ii. 11, 411). The density, however, of a sample of oil cannot be taken as a fair criterion of its value for illumination; for sometimes oils which have a high specific gravity contain a considerable proportion of light constituents, but the preponderance of heavier hydrocarbons imparts to the whole a high density.

In odour, again, much difference is observable. In some oils certain foreign matters are present in such quantity as to give to the whole quite an offensive odour. Often this is due to the bituminous material spoken of as affecting the colour; sometimes to sulphur compounds, as sulphuretted hydrogen, &c.

Passing by almost imperceptible gradations through the denser and darker varieties of petroleum, we come to maltha or mineral tar or pitch. This is generally considered as being merely petroleum in which so much bituminous matter is either dissolved or suspended as to impart a black colour and a semi-fluid viscous consistence to it. This is consequent upon the evaporation of the more volatile oil, and the subsequent oxidation of the more solid constituents. Maltha is an intermediate variety between petroleum and solid bitumen or asphalt, noticed in the article BITUMEN.

Early History.—Though the immense traffic in these bituminous substances that we now see carried on every day is but a recent feature, still these

springs and deposits have been known from very early times.

Probably the earliest account we have of the use of bitumen is found in the writings of Herodotus respecting the building of Babylon. The same narrator describes the collection of petroleum in Zante, one of the Ionian Islands, then called Zakanthus or Zacynthus. He calls this product pitch, and says that it is obtained by letting down a pole into the water, with a bundle of myrtle tied to the end. To this the "pitch" sticks. As this spring still yields as plentifully as ever, there can be no doubt that it has been flowing for over 2000 years.

Pliny and Dioscorides described the oil from Agrigentum, in Sicily, the latter specially stating its use in lamps; and remarking, with reference to the name it had gained—viz., Sicilian Oil—that "those who style this Sicilian oil commit a manifest error, because it is nothing but a species of bitumen."

In France oil springs have been known from time immemorial, at Clermont and Gabian, in Languedoc (hence the name Oleum Gabianum). Numerous springs exist also in Italy. The cities of Parma and Genoa were for a long time supplied with illuminating oil from Amiano, on the Taro, and other places in North Italy. Near Ecbatana, in Persia, was a petroleum lake, which Plutarch saw on fire. In China, Thibet, and especially in Birmah, near the Irrawaddi, are extensive wells or pools of petroleum, whose products have afforded a commodity of trade for centuries. Bakoo (or Baku), in Georgia, on the banks of the Caspian, has from distant times furnished petroleum in such abundance as to make it an article of commerce. In consequence of the numerous springs, streams of inflammable gas, and frequent eruption of mud from the "mud volcanoes," this region has been denominated the Field of Fire.

In North America, more especially in the region which now produces so large a quantity—namely, Pennsylvania — petroleum has long been known. Numerous old wells are found in Pennsylvania, Ohio, and Canada, which were probably dug by the race of people who worked the copper deposits of Lake Superior and the lead ores of Lexington, before the time of the Indians.

Geographical Distribution.—These substances are found very widely distributed over the earth. In North America and some parts of Asia immense quantities exist, whilst the supply from the other places is as yet comparatively trifling. In Europe it is interesting to note that both England and Scotland furnish small quantities.

In 1847 a spring was discovered in Derbyshire, which was successfully worked by J. Young, of Glasgow, until exhausted. The Odin lead mine, Derbyshire, contains a deposit of elastic bitumen. This appears to be the first discovery of bitumen in England, and was made by Dr. Lister in 1673. In Lancashire it is present to some extent, strongly impregnating the peat cut on Downholland moss, in the vicinity of Ormskirk. Several bituminous springs are found in Shropshire and other parts of England. In Scotland bitumen is found at the coal mines of Hurlet, near Paisley, where it incloses crystals of calcareous spar.

In France in 1840 a mania prevailed for putting bitumen to industrial purposes (M. Dumas). Bituminous schists, petroleum localities, &c., were sought for in all the provinces, and in 1843 thirty varieties were exhibited on the Bourse by different Parisian companies. Two years later the extraction and purification of their products was in full operation in various parts of the country; and in the departments of Ain, Landes, Puy de Dome, Bas Rhin, and Haut Rhin there were sixteen mines, employing 489 men, and yielding an annual revenue of nearly £30,000. This bitumen, however, did not answer all the purposes promised, and many who put capital into the undertaking were ruined.

The coal basin of Autun (Saône et Loire) contains largely worked beds of bituminous schists, from which an illuminating oil can be profitably produced by distillation.

Large quantities of mineral tar or maltha are found at Puy de la Pège, rendering the soil so viscous that it adheres to the foot of the traveller. This is also found in the Harz mountains, in Germany.

A very similar substance is that obtained from Bechelbronn, called also Stein oil, and sometimes, from its geographical origin, Strasbourg grease. It is too thick to be made of profit as an illuminator; but is applied for many advantageous purposes, particularly as a substitute for grease to lessen the friction of machinery, and also for greasing the wheels of carriages.

Seyssel bitumen is found in calcareous oolite, from which it is extracted by heating fragments of the rock in large cauldrons. This bitumen, as well as that from Parc, on the Rhone, and Lobsann, on the Rhine, somewhat closely resembles in very many particulars that from Bechelbronn.

As before stated, Clermont and Gabian have long yielded oil for illuminating purposes. Hatten, on the lower Rhine, the departments of Auvergne, Nord, and probably some others, also furnish bituminous products. Neuchatel, Switzerland, and Tagernsee, Bavaria, are said to yield bitumen, that from the former place being considered the best concrete that can be obtained.

In Italy, the oil of Amiano, in the Duchy of Parma, formerly supplied the city of Genoa with light. Springs are found also at Saint Zibio, in the Duchy of Modena, and in the island of Sicily.

South of Vesuvius a spring of petroleum was observed by M. Breislack (Laboulaye) bubbling up through the sea; here it is apparently connected with volcanic action, and the oil floating upon the surface of the water is sometimes seen at some distance from its source. The sea around the volcanic isles of Cape Verd is frequently seen covered with an oily film (Laboulaye). At Monte Ciaro, near Piacenza (Italy), naphtha is procured by sinking pits in the horizontal beds of argillite, which gradually fill with water; the oil oozes out from the rock, and floats upon the surface, from which it is skimmed off.

Dalmatia, on the north-east shore of the Adriatic, in the Austrian empire, contains large deposits of a limestone so charged with bitumen that it can be cut like soap. Arlona, in Albania, south of Dalmatia, has also furnished a considerable quantity of bitumen.

Wallachian petroleum has not yet come into extensive use, though there is reason to believe that very large quantities may be procured from that district. The first cargo reached London in January, 1864.

Galicia has attracted some attention as a source of mineral oils. In West Galicia the ground is charged with an oil almost identical with Pennsylvanian petroleum. The tract of country is the mountainous district inclosed by Limanowa, Neusandec, Grybow, Cieskowice, Gorlice, and Sbyszyce, about 20,000 hectares (nearly 50,000 acres) altogether. From here in 1866 about 268 tons were obtained. The wells need only be bored to a depth of 10 or 15 feet to yield an abundant supply. According to the reports of the American engineers and others who have visited the spot, the little river Dunajec will probably some day become the European Oil Creek. The eastern portion of Galicia yields also a smaller supply of oil, which more resembles that of Canada. Extensive refining works have been established, and several wells bored. On an average the wells yield from 70 to 140 gallons a day, though, in a few cases, 700 to over 1000 gallons have been produced daily. The oil is pumped from the wells, which are not more than 300 feet deep.

With reference to Zante petroleum, which we have already said was described by Herodotus, Dr. Paul has stated that five barrels a day may be collected from these wells; there is little doubt that if proper means were taken this quantity might be greatly increased. After careful explorations it has been found that all the natural oil springs of Greece, both in the islands and on the mainland, can be traced originally to a locality on the coast of Greece. The petroleum is found to be of good quality, and a company was formed in 1865 for the development of the property.

In the Crimea the principal Russian sources of petroleum are found, though as yet they have not been worked in such a manner as to indicate anything like their real value. The petroleum springs are entirely confined to the eastern portion, and almost wholly to the peninsula of Kertch. In some of the more clearly marked belts of country wells sunk but a few yards deep yield more or less naphtha of fair quality. The position of the petroleum is considered to be indicated by lines of different colour to the rest of the soil. In the early part of the spring these lines are greener, and in the early summer they are yellower, than the rest of the land. The whole belt of land reaches from the Sea of Azof to the Black Sea, as far as Arabat and Kaffa, and very possibly it stretches even farther to the west, extending into the steppes. The petroleum here would seem to be stored in tertiary rocks, the only rocks to be found in the region; and in consequence of the tilting up that the strata have undergone, there is not here a layer of sandstone or shale, as often seen in the American oil regions, lying over the oil-bearing rocks. On this account it is that the method of obtaining the oil differs so widely from that practised in America. Some marked, though as yet untraced, connection is seen to exist here between the petroleum springs, the salses, or mud volcanoes, and the salt lakes. All three are very abundant in this region.

The naphtha obtained from Beshevli is described as being of a deep-green colour, thin, and transparent.

The Tatars, who formerly peopled the Crimea, have sunk innumerable small wells, which are mostly found in narrow bands, extending usually along the axis of east and west valleys, midway between the limestone cappings of the north and south.

It is found that when the modern sinkings are in the line indicated by the pits of these Tatars a yield may be expected; whilst in most cases where a deviation is made from this course oil is not found in the immediate vicinity. One, bored 500 feet to the north of the line of "oil crop," yielded no trace, whilst in the line itself were twenty or more modern sinkings, all of which were more or less successful (Ansted).

Passing now into Asia, we find that an immense petroleum district exists in the immediate vicinity of the Caspian Sea. Baku, in Georgia, on the west shore, has been already mentioned as having been celebrated from early times for the inflammable gas and naphtha naturally exuding from the soil. The oil region here embraces a tract of country about 25 miles long and half a mile in width, in the neighbourhood of hills of volcanic rock, from which the heavier sorts of petroleum ooze out. Large open wells are dug into this tract, which consists of a porous argillaceous sandstone belonging to the tertiary period, from 16 to 20 feet in depth, into which the oil slowly flows from the surrounding and subjacent strata.

It is observable that the oil which is collected from the centre of the tract is very clear and pure, and is generally alluded to as native naphtha. That, however, which is obtained from the sides varies in colour and consistence, being heavier and darker coloured the farther from the centre; that which is obtained at the margin of the tract being solid asphaltum.

Kinnier says that "some of these wells yield 1000 to 1500 lbs. a day." They are in a certain sense inexhaustible, for they are no sooner emptied than they again begin to fill, the naphtha continuing to flow in till it has attained to its former level. The natives use it as lamp oil, and also for cooking purposes. The Russians commenced working these springs in 1858.

Upon the east shore of the Caspian, also, the store of bituminous products is no less considerable. These have been only recently worked systematically, and the supply seems almost without limit. The wells are frequently side by side, and seem to be unaffected in many cases by another being dug

in the immediate vicinity; one, the flow from which had yielded 3400 lbs. a day, not being materially altered by the digging another close to it, from which 40,000 lbs. daily were obtained. Since the American method of boring has been adopted the quantities have been very much increased, the oil being driven up from a depth of 250 feet below the surface with such force as to spout from 50 to 65 feet in the air.

Leeds remarks that this vast bituminous formation has its origin to the northward, in the Isles of Naphtha, which are situated on the eastern shores of the Caspian. It stretches away to the westward for over 100 miles, reappears, on the western shore, in the vicinity of Baku, and terminates in the hills of the Crimea.

This Persian naphtha would seem to be of two sorts, distinguished sometimes as black and white naphtha. The former, found around Kerkook, ordinarily resembling pitch, is used by the natives on the banks of the Euphrates and Tigris for covering the bottoms of the vessels which navigate those rivers, and also as lamp oil. The white variety is quite different, is much thicker, and described as being more like tallow than anything else. It affords a better light, and emits a less disagreeable odour than the other. It floats like a crust on the surface of the water. A fountain of this is found at the foot of the mountains of Buctiari, half way between the city Shuster and the valley of Ram Hormouz. (Kinnier's "Geographical Account of Persia," p. 39).

The principal petroleum regions in Birmah are those near the towns of Yeynangyoung and Pagan. There are now 150 wells worked at Yeynangyoung, which yield 15,000 viss daily (a viss about equals $3\frac{1}{4}$ pints), an amount equal to 6000 gallons. The total yield is about 9375 tons per annum. In Pagan there are fifty wells, which daily yield 1500 viss of oil, which the earth oil contractors are allowed to purchase. These wells yield a more liquid oil, which more resembles naphtha—of a blackish nature—and better suited for light than Yeynangyoung oil. The total supply of petroleum now in Upper Birmah is $10{,}312\frac{1}{2}$ tons annually. This is usually known when purified as Belmontine. When this is purified by distillation the more volatile portion of the distillate is separated, and used as a solvent for grease, &c., under the name of sherwoodole.

Though, as we have seen, various countries of the world produce supplies of these valuable commodities, the vast quantities of petroleum annually exported from North America show us that that Continent must be emphatically considered the storehouse of the world for these bituminous products.

In South America comparatively small quantities are found, and these are principally deposits of solid bitumen. The countries of Venezuela, New Granada, Ecuador, and Peru contain some of these deposits. Payta, in Columbia, Magdalena, and Coxitambo, near Cuença in Ecuador, are also named as small sources.

Some of the islands of the West Indies have been known as sources of asphalt for a very long period, Cuba and Trinidad more especially. In the eastern portion of the latter island petroleum springs are found between Holguin and Mayari, and also in the south-west, near Santiago de Cuba. A single locality of bitumen occurs in the island of San Domingo; this is about three miles north of the town of Azua. A little bitumen is found in Barbadoes, and also a small quantity of a greenish petroleum; indeed, one of the names that is frequently borne by this substance, viz., Barbadoes tar, is a reference to this geographical origin.

The "Great Pitch Lake" of Trinidad, already mentioned in the article Bitumen, is 99 acres in extent, and contains millions of tons of asphalt. This is justly considered the most wonderful, as it is the largest, deposit of asphalt in the world. It is situated on the west shore of the island, about midway from its northern to its southern extremity.

The North American Oil Regions.—A small quantity of petroleum had been found floating for time immemorial on the surface of a pool on the premises of Messrs. Watson & Co., lumber dealers of Titusville, Crawford Co., Penn., and it was the custom to collect this for medicinal purposes by absorbing it in blankets. A company, originated by Messrs. Eveleth & Bissell, and designated the Pennsylvania Rock Oil Company, was set on foot in the autumn of 1854 for turning the oil to practical account as an illuminating agent, and for lubricating machinery. In the winter of the same year Professor J. B. Silliman, jun., analyzed the oil, and reported so favourably upon it that the company's stock was bought up freely. For several years, however, the enterprise did not answer, and in 1858 Colonel G. L. Drake, the superintendent of the company, was fortunate enough to conceive the plan of boring the land that had already given so large a surface production of petroleum. He continued his operation of boring, to the amusement of his friends, into 1859, and on the 26th of August of that year "struck oil" at a depth of 71 feet. The drill sank suddenly into a cavity in the rock, and the oil rose to within 5 inches of the surface: 400 gallons a day were obtained at first, but a larger pump having been substituted for the small one then in use, the supply was increased to 1000 gallons daily. This amount was obtained regularly without interruption for several weeks. The excellent quality and abundance of the oil, which sold for 55 cents a gallon, gave, as may be imagined, great value to every spot of ground in the vicinity, as well as to all those places whence oil had ever been obtained, or which were considered likely to produce it.

The creeks in the vicinity were soon explored, and before the close of 1860 there were 2000 wells in this region, and 74 of these produced 1165 barrels daily, or 46,600 gallons, each barrel containing 40 gallons.

The most important oil regions of the United States are undoubtedly those of the three contiguous states—Pennsylvania, Ohio, and West Virginia. Besides these Kentucky, New York, Michigan Indiana, Illinois, Tennessee, Colorado, Oregon,

Montana, and California have been indicated as yielding more or less of this valuable product; in fact, there is hardly a state in the union that has not produced some. In Pennsylvania the oil region is confined to the north-west portion of the state, the most productive wells being those of Oil Creek; some of these have discharged 500 to 2000 barrels of oil daily, and one as much as 3000 barrels.

The total yield of petroleum from the whole Pennsylvanian oil region during the years 1861–62 had an average of 8000 barrels a day. The West Virginian and Ohio supplies, though not by any means so plentiful as those from Pennsylvania, average a much greater density, and command a higher price as a rule.

In California the springs of thick and tarry petroleum are usually accompanied by surface collections of asphaltum. The largest of the natural wells here is about 30 feet in diameter, and is situated, together with several smaller outflows, in the midst of a great field of asphaltum, which is estimated as being equal to a square mile in extent, and a yard deep. The wells are filled with the thick black oil, which is kept in a constant state of ebullition by the escaping marsh gas. A similar bituminous deposit exists in Mexico.

The oil-bearing strata composing this great oil region are situated between the middle of the carboniferous system above, and the Hamilton shale, which directly overlies the corniferous limestone below, that of North-western Pennsylvania standing higher than that found in West Virginia and Ohio.

In the former district we find lowest the shales and limestones of the Portage group, yielding oil to the deepest wells on Oil Creek. At this place these rocks have a thickness of 1700 feet. Above them alternate the argillaceous shales and sandstone, the latter being sometimes replaced by limestone, which form the Chemung group.

A record of a well sunk in this region is taken from the note-book of Mr. Leeds. The well was situated on the Alcorn Farm, Alleghany River, about 3 miles from Oil City, county Venango (the "heart of the West Pennsylvanian oil region:")—"75 feet of a very soft rock, of the nature of gravel, very soft. 75 feet of a rock, called by the drillers 'soapstone.' It is in reality an argillaceous shale. It has a somewhat grey colour, and is harder than the preceding rock. 10 feet of sandstone, known everywhere as 'first sand rock.' 75 feet, another series of shales distinctly argillaceous. 20 feet 'second sand rock.' 200 feet argillaceous shales. 15 feet 'third sand rock.' 80 feet argillaceous shales, which the man who was boring described as 'shelly,' meaning that they were in thin layers of alternately hard and soft rocks."

The total depth of the oil-bearing formation of this region, and that in West Canada, may be taken at about 6850 feet, composed of—

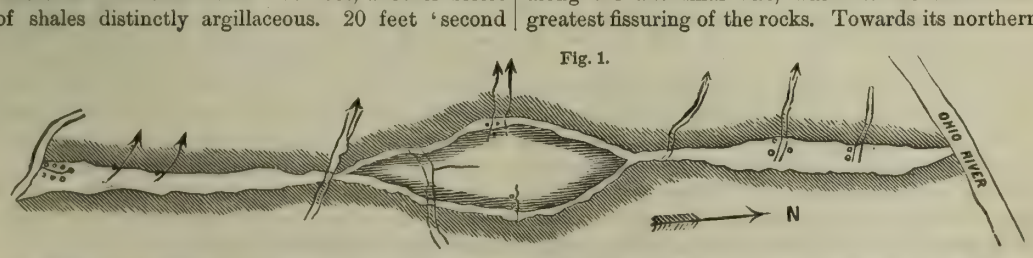
50	feet of	Corniferous limestone,		
100	"	Marcellus slate,	Middle	Devonian.
1000	"	Hamilton group,	Middle	Devonian.
300	"	Genessee slate,	Middle	Devonian.
1700	"	Portage group,	Upper	Devonian.
1200	"	Chemung group,	Upper	Devonian.
800	"	Lower coal measures,	Carboniferous.	
1000	"	Middle "	Carboniferous.	
700	"	Upper "	Carboniferous.	
6850				

In Canada there are two oil regions, one in the peninsula of Gaspé, the most easterly point of Canada East; the other, the most important, around Enniskillen, to the south of West Canada. The geographical and geological relations of these tracts are treated at length in the "Report of the Geological Survey of Canada"—volume for 1863.

Oil springs are also to be seen in Canada, along the banks of the Thames for a distance of about four miles, in the township of Oxford and Mosa. Near Tilsonburgh, in Dereham, two wells were sunk in 1861. These sources have, however, yielded very little oil.

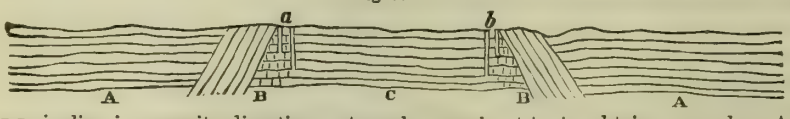
Geological Distribution.—It will thus be seen that, though throughout other parts of the world the more recent rocks and formations yield petroleum, yet in America the oil-bearing rocks are found usually in Palæozoic formations. In California, it is true, the oil tracts are spoken of by Professor Silliman as being pretty certainly cretaceous or tertiary; and the bitumens of Venezuela and of the island of Trinidad are said to be not lower than the Miocene in the tertiary formations. Still we must consider these as simply exceptions to the rule, and admit that in general on this continent the more fluid bitumens are not to be found in higher geological strata than the coal measures. The oil wells are usually most productive when sunk in the course of an anticlinal. Thus, E. B. Andrews, in speaking of the West Virginia oil field (*Amer. Jour. Science*, vol. xlii. pp. 34), says that all the productive oil wells in this part of the state group themselves along the anticlinal line, which is the one of the greatest fissuring of the rocks. Towards its northern and southern extremities this line presents the form of a simple anticlinal, with dipping on either side of the axis at angles varying from 5° to 25°; but in the middle part there is a double fracture, the lines of dislocation inclosing a somewhat elliptical-shaped area about 10 miles long by 1 wide (Fig. 1.).

Fig. 1.



A section of the dislocated strata is shown in Fig. 2. The horizontal rocks, A A, belong to the higher strata of the coal measures. The dislocated strata,

Fig. 2.



B B, incline in opposite directions, at angles varying from 30° to 60°, and have a probable thickness of about 800 feet. Above C we have the horizontal strata within the break; the rocks belong to the lower coal measures, and have been more or less flexed by lateral pressure. The most valuable West Virginian wells occur in this middle part, C; those in A A and also in B B have not yet yielded any oil. The latter do not appear to have been much fissured in the disturbance which occasioned this anticlinal, but rather to have been lifted up bodily. There are several advantages which this central portion possesses. 1st. It is many hundred feet lower in the geological series than the rocks on either side, and consequently so much nearer the probable sources of the oil, viz., the Devonian rocks. And 2nd. The strata here are bent and more or less fissured; and again, it is probable that the disturbance and fissuring which occur here are not confined to these surface strata, but penetrate down to the underlying Devonian strata, thus allowing every facility for the ascent of the oil.

The presence of these fissures would thus seem to be necessary if oil is to be obtained in any quantity; for they "give space for the formation and expansion of the hydrocarbon vapours," and also furnish receptacles for the condensed oil. That they are connected with the deeper oil sources is shown by the varying condition of the crude product. If they have any surface outlets, the oil within them is thicker, more viscid, and of greater specific gravity, in consequence of the gradual escape of the more volatile ingredients. Thus, by reason of the greater or less evaporation that has taken place, we have oil of all degrees of consistency; as might be imagined, that from shallower wells being thickest, since the fissures which these wells strike will be more likely to have surface outlets than the deeper fissures.

In the anticlinal whose course we have followed, these fissures occur most abundantly just within the line of fracture; consequently more numerous and more productive wells are found here than at any other points.

As a rule, the contents of these fissures, or "pockets," as they have appropriately been termed, are petroleum, water, and uncondensible gas, these placing themselves in the order of their gravities—the water being lowest, above this the oil, over which the gas is retained, usually at very considerable pressure. This being so, it will be seen that a more or less vertical fissure may be "struck" at either portion, and either gas, oil, or water at first obtained.

If the portion containing oil be entered, this may by the pressure of the gas above be forced up to the level, or even spout many feet above the surface. By the increase of space afforded by its escape, however, the expansive force of the gas will in a short time be expended; and then artificial means, pumping, will be resorted to to obtain a supply. At first by this means the product will simply be oil; but eventually, when its supply begins to diminish, oil and water will probably flow.

If the drill enter the cavity containing gas, this will at first escape with great rapidity; then the water rushing in from communicating fissures below, will force the oil into the lower end of the pipe; this may then be pumped out, and finally a mixed product will be obtained.

When, again, the boring penetrates that portion which contains water, the first result will probably be an upward rush of water by the expansive force of the imprisoned gas, which, unless the gas has spent its power in driving out the water, will be followed by a similar rush of oil, as soon as the latter is forced down to the level of the vent hole. If, however, the power of the gas is not adequate to this, by pumping, the junction of water and oil may be kept even with or below the lower end of the pipe, and so either oil or a mixture of oil and water may be obtained.

The facts adduced with regard to the Canadian borings would show that the cavities containing oil cannot have a great horizontal extent, but must be more or less vertical in general direction; for there can be no doubt that the number of cases in which adjoining wells interfere with one another is comparatively small. The qualities of the oil, too, from contiguous wells often vary very much; and borings made in the same region, whether in horizontal or upheaved strata, are very seldom any two of them of the same depth, so that from the position of these cavities the chance of striking oil is but small even in these oil regions themselves.

Professor Evans, concerning this, says:—"It is one chance out of many to strike oil at all, even in the neighbourhoods where it exists in abundance. The drill as it enters the cavity sinks variously from 4 to 5 inches to as many feet, sometimes sticking fast, as if between the oblique sides of a narrow fissure. But there are facts connected with the history of oil wells, particularly their intermittent action and their interference with one another, which serve to show the existence in many cases of systems of cavities connected together by channels of communication more or less free, running sometimes along the strata and sometimes across them. The productiveness of a well depends upon its entering either one of its main reservoirs or some one of its important connections."

Indications of Petroleum.—Those accustomed to petroleum boring look for certain natural signs or indications which they consider point to the fact

that petroleum is to be found in the region. There are no infallible criteria by which they may be assured of its presence in sufficient quantity to prove remunerative; but experience has shown that where certain phenomena present themselves, the existence of oil in the region is rendered a very strong presumption. These signs we might characterize as geological and oil indications proper. Amongst the former it is necessary to take into account the nature of the formation, to consider whether in other places oil has been obtained in quantity from it, and the fact of lines of upheaval of the strata; these affording evidence of disturbance, which is likely to have left cavities or gaps, serving as reservoirs of oil. With these we might also class the presence of salt water springs, which, though their direct connection with petroleum cannot be traced, are, nevertheless, almost constantly found in all the great oil regions; and, in fact, as we have seen, the first accounts we have of petroleum in America mention its discovery when boring for salt water, and indicating the continual source of annoyance it was to those thus engaged.

The more important oil indications proper are gas springs, oil springs, surface collections of bitumen, surface collections of oil, either impregnating the soil or floating upon stagnant pools, and the so-called show of oil obtained during the process of boring a well. With reference to the first, it is by many considered that the presence of a jet of inflammable gas, whether constant or intermittent, issuing from a fissure in the rocks, coming up with a water spring, or exuding from the soft soil, affords a most valuable indication of petroleum. It is almost certain to consist either wholly or in great part of marsh gas, the connection of which with petroleum we have already noticed. It is this connection between the two that makes its presence valuable as a "sign;" and therefore before any gas spring is held as evidence of the presence of oil, it must be shown to be inflammable; for, as Richardson has pointed out, carbonic acid gas is a very frequent exhalation from the boggy marsh lands of West Virginia and other parts of the United States, and must not be considered of any value as an indicator. The probability is that oil will be found in the rocks below such an inflammable jet; but this is not necessarily the case, for gas is believed under certain circumstances to travel laterally by communicating fissures, occasionally for some distance. On this account, before boring it is necessary to consider well the "nature, position, and peculiarities of the surrounding and subjacent rocks," so as to determine the probable place of the oil fissures or basins.

Of course, since the water and oil which such fissures contain tend to seek their own level, these will be more likely to flow laterally than the gas, so that the existence of a cavity at some distance from such a jet is rendered rather improbable. On the other hand, Professor Hunt remarks about the West Canadian oil wells, that "the inflammable gas which issues from the wells is not necessarily connected with the petroleum, inasmuch as it is an almost constant product of the decomposition of organic matters, and is copiously evolved from rocks which are destitute of bitumen. It is similar to the gas of marshes and the fire-damp of coal mines." The character of the jet and the quantity evolved must therefore be considered before it be taken as any indication of petroleum. It is well to remember here that this marsh gas is almost always found to accompany bituminous products in all parts of the world. The jets at Baku, in the Crimean oil region, and in the West Indies, may be instanced as examples of its very general presence in large quantities in these oil-producing tracts.

Another important indication is the presence of oil floating on pools or streams, or oozing from the soil or rock-crevices; this, technically known as "surface oil," is a sign very commonly sought for in the great American districts. It is liable to error both as to the amount and position of the oil; for sometimes rocks from which petroleum oozes are composed of a limestone impregnated with a bitumen more than usually fluid, and when floating oil is met with it has often been carried by the water to a very considerable distance from its source.

The surface bitumen often surrounding oil springs which may be flowing or have ceased, the springs themselves, whether of oil simply or water springs with which oil also ascends, are considered indications of more or less value; but though they certainly show that oil has been or is accumulated somewhere beneath the surface, they do not say anything as to the distance at which such a supply may be, or at what depth it may be found.

Formerly it was considered a valuable indication to obtain a little oil from the upper strata when boring the wells; now, however, in consequence of the fact that large wells have often had no preliminary show of oil, whilst in other cases, when the "show" has been abundant, it was merely superficial, and unconnected with the deeper and larger supplies, this is not regarded as at all decisive for a successful result. According to Professor Evans, the value of this test varies with the depth, it being of greater value with the greater depth at which the oil is obtained.

In most cases the landowner leases for thirty years the right to raise the oil, and such right of way as may be necessary, for a royalty of from one-tenth to one-half the oil. A bonus of from 5000 to 10,000 dollars is also sometimes paid to the landowner. The lessee binds himself to begin operations within sixty days. If he fails to prosecute the work either to success or abandonment within a reasonable time after beginning, the lease is forfeited.

In West Virginia the value of petroleum lands upon which indications have been found varies from 200 to 1000 dollars per acre. In Venango county, Pa., the heart of the oil region, the lands on the creeks are worth 1000 dollars an acre. In less highly appreciated spots 100 to 300 dollars per acre may be obtained. These lands were worth about twenty dollars, or less, per acre, previously to the discovery of petroleum.

*Well Boring.**—The site of the proposed well being selected, a frame of timber called a "derrick," 40 feet high, formed of four posts, inclining towards each other at the top, set upon a frame of logs 8 or 10 feet square, or sunk into the ground, is set over it. These derricks are prominent objects in the landscape of an oil region. At the top of the derrick is a pulley, over which a rope is passed when the boring tools or tubing are to be hauled up. A steam-engine, usually of six or ten horse power, is placed near the derrick, and its power is applied by means of a belt from the fly-wheel of the engine to a large wheel and crank; the crank giving motion to a walking-beam, at the end of which boring tools or pump-rods are attached, as may be required. The lower part of the derrick is closed in sometimes with boards.

The first thing done is the driving in of the soil-pipe. This pipe (Fig. 3) is 4 inches in diameter, made in 10 feet lengths, fitted at the ends, and driven by means of a heavy block of wood as in pile-driving. The lengths follow each other in succession until the rock is reached. This is sometimes 30 feet below the surface, and the soil-pipe has to penetrate earth, sand, and loose slate, &c. The drilling tools are attached to each other by means of a screw connection in the following order:—Bit (Fig. 4), or reamer (Fig. 5); auger stem (Fig. 6); jars (Fig. 7); sinker bar similar to auger stem, but shorter; rope socket (Fig. 8), to which the rope is attached at one end, and at the other to the temper screw (Fig. 11). The annexed diagram gives the position of the engine, walking-beam, and connection, as they are commonly arranged, together with the relative positions of the boring tools when in use (Fig. 16.).

The temper screw is attached to a rope which connects with the end of the walking beam, and serves to regulate the descent of the drill without the inconvenience of lengthening the rope at short intervals. The sinker bar gives weight to the upper

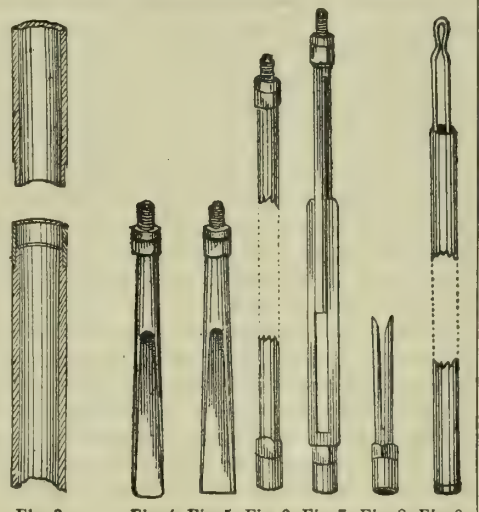


Fig. 3. Fig. 4. Fig. 5. Fig. 6. Fig. 7. Fig. 8. Fig. 9.

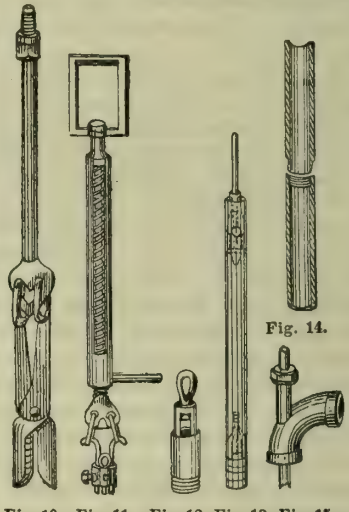


Fig. 14.

Fig. 10. Fig. 11. Fig. 12. Fig. 13. Fig. 15.

part of the jars, which slide together, and the auger stem and bit afford weight to do the drilling. The downward stroke of the walking beam releases the auger stem and bit for an instant as the jars slide together, and they fall the distance necessary to penetrate the rock, and are again lifted by the jars on the upward stroke, falling again as the stroke descends.

The soil pipe is cleared of its contents by the tools and sand pump (Fig. 9), which is a hollow tube with a valve at its lower end. This permits it to fill with the finely pulverized detritus made by the drill, and it is alternately lowered into and raised from the well and emptied, until the well is clear for the tools again. When the soil pipe is clear, drilling the rock is begun in the way described. An ordinary set of tools weigh 900 or 1000 lbs. A circular motion is given to them by means of a lever passed through the rope near the temper screw at the top of the well, and moved round gradually by one of the workmen. The reamer is used to enlarge the hole made by the bit.

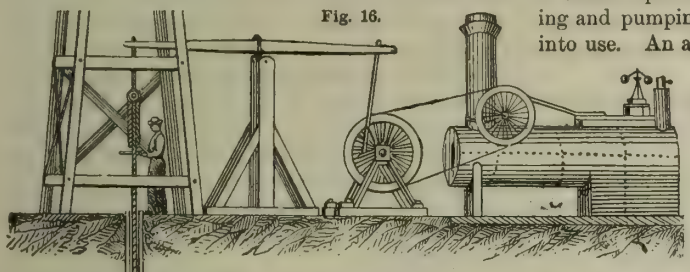
Occasionally, in drilling, the tools will enter a crevice in the rock and become wedged so tightly that they are often lost for want of means to extricate them. Numerous appliances have been invented to accomplish this. The "lazy tongs" (Fig. 10) is one of these. It is attached by a screw pin to the sinker base, or other suitable rod of iron, and lowered so as to catch the end of the missing tool in its jaws. It is said by the workmen that to sink 100 or 200 feet is comparatively easy, but that at 400 feet the risk of loss of tools is much increased. At that depth the jar of the falling bit and auger stem is not nearly so perceptible at the well top, the elastic rope taking it up. The well having been sunk to the oil, which does not always manifest itself by flowing, it is tubed with 2 inch wrought-iron pipe

* Our accounts of this and of some refining operations are abstracted from Gesner's Treatise on Coal, Petroleum, and other Distilled Oils, to which we are also indebted for many of the accompanying illustrations.

(Fig. 14) fastened together by screw joints in 10 or 12 feet lengths.

The first length sent down is the brass or iron cylinder, which constitutes with its valves the "oil pump" (Fig. 13). This is about the same size as the well tube, and has at the bottom a ball valve fitted into a brass plug having a screw top. The pump rods, which are tough wooden rods fitted

Fig. 16.



together by iron sleeves and screws, connect at the lower end with the upper valve of the oil pump, which has a screw socket at its lower end, so that it can be lowered down to the bottom valve, screwed over its top, and pulled up when necessary.

The dotted lines of the oil pump (Fig. 13) show the position of its valves when the up stroke is at its highest pitch. When the oil pump is adjusted, the required lengths of tubing are connected one by one and the tube lowered into its place. In some wells a strainer of wire cloth is placed round the lower part of the oil pump. The pump rods work through a stuffing box (Fig 15), which is screwed to the top of the well tube. The oil pump is not allowed to rest on the bottom of the well.

To prevent communication between any particular portion of the well and the tube, a bag of linseed, called a seed bag, is sent down to the required place. This bag, encircling the tube, soon swells by the water which is always present, and forms a water-tight joint in the well. For instance, when it is desirable to prevent the water beds from one of the upper rocks from flooding the oil bed of the lower strata, the seed bag is inserted below where the water is supposed to be, and prevents it from reaching the oil pump at the bottom of the well. For drawing the tube a "swivel" (Fig. 12) is used. It screws into the tube.

When the soil is not deep, a circular excavation is made down to the rock bed, and a hollow log or "gum," as it is called, placed in it on one end. The base is surrounded with clay to prevent the influx of surface water. The seed bag is also used to keep the lower part of the well free from water.

When steam engines are not to be had conveniently, a spring pole is used to give the proper motion to the boring tools. It is worked by two men, while another gives the circular motion to the tools by turning the lever at the top of the rope.

Some improvements have been suggested in drilling and pumping, which are in some places coming into use. An air pump is sometimes used to force a current of air through a tube carried to the bottom of the well tube, and in this way compel the oil and water to flow out without the use of pumping rods and valves. The improvements in drilling are designed to remove the detritus without the loss of time and the inconvenience of using the sand pump, and to bore the well with an auger instead of a trip hammer motion.

Under favourable circumstances the wells are sunk at the rate of 6 or 8 feet per day.

A drilling apparatus has been invented which has the bit shank hollow. The bit itself has three cutting edges formed by stout pieces of steel, set so as to radiate from a common centre. In the angle formed by these pieces, which are 3 inches deep, and where they join the hollow shank or stem, there are brass valves which permit the detritus to enter the stem. In this way it is proposed to combine the drill and sand pump. This drill is, with its auger stem, worked by a wire-rope, which is passed through an upright shaft at the top of the well.

The cost of sinking a petroleum well 600 feet is estimated at 7000 dollars; but an allowance must be made for contingencies, loss of tools, &c.

In many cases, especially during the first year or two of the petroleum working, 1858 to 1860, pumping has not been needed at first; the force of the imprisoned gas being sufficient to cause the oil, alone or mixed with water, to rise like a fountain. Many thousand gallons have been wasted for want of proper provision for such an occurrence as this; and on more than one occasion disastrous accidents have followed the ignition of the petroleum vapour that thus impregnated the atmosphere near the well's mouth.

Nothing can be more capricious than these "flowing wells," the oil supply varying with age, proximity of other wells, &c., in such a manner as sometimes to lead the most experienced oil miner completely astray.

A short account of the Enniskillen wells will illustrate this. The great "Shaw" well began to flow in January, 1862, and when oil was struck the flow was too great to be accurately estimated; when it was controlled it amounted to over 55 gallons a minute. This well continued to flow spontaneously for ten months.

Some time after the Shaw well flowed so successfully, a second well was bored into the rock to the same depth at about 100 yards distance; this yielded

a copious discharge of oil; but this second well had the immediate effect of reducing very materially the flow from the Shaw well. When either was plugged the other yielded a full discharge; but when both were allowed to flow, each gave only a partial supply. A third party, owning a small lot between the two wells, commenced boring on a line drawn from the one to the other, at a distance of 30 yards from the Shaw, naturally expecting to rob both wells. In fact, however, this third well proved an utter failure, though the rock was bored to a much greater depth than the other two wells.

In the middle of 1863 the supply had entirely ceased, a total yield of about 35,000 barrels having been obtained. Within a year from the boring of this (Shaw) well thirty more had been sunk in the neighbourhood, and at the period of the greatest activity as much as 12,000 barrels a day was produced in this region. Of these wells, before the close of the year, all but two had ceased to give any oil, and the total supply from these was but 400 barrels daily. One of the wells, sunk 200 feet, when first opened yielded 2000 barrels in twenty-four hours.

A curious fact has been noticed regarding the stoppage of the discharge of oil from these wells. The deepest wells have invariably been those which have first given out, and the two out of the thirty above-mentioned which are now flowing are the two shallowest. Thus in nine wells the depth was as follows:—

Well G,.....	230 feet in the rock.	
" I,.....	208 " "	
" B,.....	200 " "	
" C,.....	182 " "	
" H,.....	180 " "	
" D,.....	162 " "	
" A,.....	158 " "	
" E,.....	109	At present flowing.
" F,.....	109	

G failed first, after discharging only 4000 barrels. I failed next, then B and C, then H and various intermediate wells; and the only old well now flowing is F, at a depth of 109 feet under the rock surface; and E, recently made, within 20 or 40 yards, and to the same depth in the rock, yields a copious supply. It must be remembered that the depths under the rock surface are given, since this is very even; whilst the surface of the ground above is very uneven, the depth of the clay varying from 40 feet in the flats of the creek to 80 feet on the banks.

No indication is given when the wells are about to cease discharging oil. The fact is known merely by the liquid flowing from the bore suddenly changing its character, and instead of petroleum salt water issues. In many cases the regular flow from the wells consists of oil and water, the latter being almost invariably saline in the deeper ones; others, when recently opened, yield petroleum only, and after a while water accompanies the oil.

Crude Petroleum—*Qualities.*—The first oil obtained from a well is usually very impure; earth, sand, water, and other foreign matters, often occurring mixed with it. After a short time, however, all these substances cease to accompany the flow, except water, which generally continues with the oil, its proportion relatively increasing with the age of the well.

This mixed product is pumped into tanks capable of containing 30 to 1000 barrels, where it is allowed to rest, and soon the oil, rising to the surface, assumes its characteristic colour. The products from different localities vary much in tint. In the Oil Creek region a greenish hue commonly prevails, though very light samples often have a reddish tint. Here, as in other places, the products of different wells differ slightly in specific gravity, those from deeper wells being lightest. The amount of dissolved bitumen which those oils obtained from the bituminous coal-fields contain gives to them a dark-brown colour. This is seen from W. Virginia and S.E. Ohio, and also occasionally in the West Canadian product.

The accompanying table of the density and colour of the oil from some of the best known localities is from Dr. Chandler's report on petroleum oil to the health department of New York city—

Locality.	Specific Gravity	Colour.
Oil Creek, Pennsylvania,..	·782 to ·804	Greenish-brown.
Pithole Creek, " ..	·745 to ·778	"
Alleghany River, " ..	·824 to ·848	"
French creek, " ..	·864 to ·881	"
Burning Spring, West Virginia,.....	·804 to ·808	"
Enniskillen, Canada, ...	·804 to ·808	Blackish-brown.
Mecca, Ohio, ...	·881 to ·891	Yellow.
Amiano, Italy, ...	·773 to ·898	Red to straw.

A very heavy lubricating oil is obtained from several wells in Ohio and Pennsylvania, of specific gravity ·860 to ·880, or even higher. Some of these heavy oils, as the "Mecca oil," remain fluid even at very low temperatures.

An oil is obtained from the wells of the Tarentum Oil, Salt, and Coal Co., of specific gravity ·795, which is of a dark amber colour, and will burn for a time in lamps without being previously refined.

A very heavy oil is obtained from near Crestline, Ohio. This resembles the "Mecca oil." The wells at Franklin, Pennsylvania, produce heavy oils. Oils which are quite equal in colour to the best refined paraffin oils are found on Duck Creek, Ohio, and Smith's Ferry, Pennsylvania.

The crude oil of Enniskillen is not by any means so pure as that from the Pennsylvanian oil region; in fact, it has such an abominable odour that at one time it was feared that this would prevent its ever coming into general use. By the improved methods of purification now employed, however, this is almost entirely removed, and the refined product is no more objectionable than the oil from any other of the North American sources. The alliaceous odour which the crude oil possesses is probably due, in some part, to some sulphuretted compound; for when it is rapidly decomposed at a red heat, the gas produced is invariably found to contain more or less sulphuretted hydrogen.

This Canada oil is sometimes very heavy, its density reaching ·820 to ·850 (NORMAN TATE), or even ·860 to ·880 (GESNER).

The influence of depth upon the physical characters of the oil is well shown in a paper by Mr. JOHN F. CARLE, of the Geological Survey of Pennsylvania. He says, "These oil-producing sands form a group of themselves, with well-defined beds of slates and shales at least 100 feet in thickness, both above and below it; and whether composed of three members, as on Oil Creek, where they were named first, second, and third sands, or split into five or six members, as they usually are to the south-east and east of the central line of the group, they all lie, as a general rule, within a vertical range of 350 feet. Each one of these three sand rocks, when they lie in clearly defined beds, furnishes an oil peculiar to itself; the first sand, a heavy lubricating oil of 30° to 35° gravity (·870 to ·843 specific gravity); the second sand, an oil of about 40° gravity (specific gravity ·819); the third, the usual light oil of from 45° to 50° gravity (specific gravity ·795 to ·773). But while each sand has its own characteristic production, the oil varies somewhat in colour and gravity in different localities in the same horizon. Thus, the third sand produces a green oil from its lower member and a black oil from its stray or upper member, where the rocks lie in their normal positions, as on Oil Creek; but where the stratification varies—thus changing the relations of the several members to each other, both as to thickness and composition—the oil is changed in colour accordingly.

"At Pleasantville, where the lower member is thicker than the upper, but fine and muddy, and the upper, or stray, is coarse and gravelly, and produces the oil—its colour is nearly black. At Pithole, Cash Up, and Fagundus, where the lower has fined down to a thin layer of argillaceous flags, and the upper member thickened into a pebbly sandstone, the oil is of a lighter colour."

The various proportions of light and heavy constituents found in the crude oil from various localities are in accordance with the above; some proximate analyses are given below, others will be found in the section in which the chemistry of petroleum is more fully dealt with.

M. VOHL has analyzed Rangoon oil. The sample was of specific gravity ·885, and yielded on distillation and rectification—

	Per Cent.
Illuminating oil, specific gravity ·830...	40·705
Lubricating oil, ...	40·999
Paraffin fusing at 60° Fahr., ...	6·071
Asphalt.....	4·605
Loss (probably light oils uncondensed),..	7·620
	100·00

Dr. SHERIDAN MUSPRATT found Canadian petroleum (Enniskillen oil) to yield—

	Per Cent.
Light coloured naphtha, specific gravity ·794,	20
Heavy yellow naphtha, " ·837,	50
Lubricating oil, rich in paraffin, ...	22
Tar, ...	5
Charcoal, ...	1
Loss, ...	2
	100

Some Californian petroleum, of specific gravity ·927, was found by J. H. WHITE, of San Francisco, to yield—

	Per Cent.
Illuminating oil, specific gravity ·813, ...	38
Lubricating oil, " ·921, ...	48
Pitch, ...	10
Water, ...	4
	100

GILBERT states that the Californian product loses 10 to 15 per cent. by volume in rectifying, and gives this analysis—

	Per Cent.
Light oil (naphtha), specific gravity ·713,...	5
Burning oil, " ·869 to 860,	50
Light machine oil, " ·898,...	25
Heavy oil and paraffin, " ·944,...	25

Some Barbadoes tar, examined by C. HUMFREY, was of a dark brown colour, very viscid, with a specific gravity of ·940. It gave—

	Per Cent.
Water, ...	5
Crude oil, No. 1, specific gravity ·912, ...	50
" 2, " ·927, ...	40
Coke, ...	5
	100

No. 1 when refined gave four-fifths of its weight of a fine pale, sweet oil, of specific gravity ·908. No. 2 yielded three-fifths of its weight of a dark coloured oil, which had a slight empyreumatic smell; its specific gravity was ·918.

NORMAN TATE examined a sample of African petroleum imported from one of the Red Sea ports. This was of a dark brown colour, faint and somewhat pleasant odour; specific gravity ·912. It commenced to give off inflammable gas at 180° Fahr. It yielded on distillation—

	Per Cent.
Oil suitable for illuminating purposes, specific gravity ·835, ...	30·0
Heavier oil for lubricating purposes, specific gravity ·887, ...	59·5
Paraffin, ...	5·2
Coke, ...	3·7
Loss, ...	1·6
	100·0

The same chemist has selected the following from a large number of analyses, as showing the average composition of most of the petroleum imported into this country from Canada and the United States. The specific gravity of the spirit and burning oil he fixed at ·735 and ·820 respectively; these being in his opinion the best points at which to fix the limits between spirit and burning oil, and between burning oil and lubricating oil.

No. 1 was Pennsylvanian petroleum. Colour, dark greenish; odour, strong and ethereal, but not unpleasant. An inflammable vapour was evolved at ordinary temperatures.

No. 2. Pennsylvanian. Colour, dark greenish; odour somewhat unpleasant. Yielded inflammable vapour at ordinary temperatures.

No. 3. Canadian. Colour dark brown; odour powerful, resembling garlic somewhat. Evolved inflammable vapour at ordinary temperatures.

No. 4. United States petroleum (locality unknown). Colour, dark greenish; odour, faint and pleasant. Yielded inflammable vapour at 86° Fahr. (not under).

	1.	2.	3.	4.
	Sp. Gr. ·802.	Sp. Gr. ·815.	Sp. Gr. ·835.	Sp. Gr. ·820.
Spirits, sp. gr. ·735, ..	14·7	15·2	12·5	4·3
Lamp oil, sp. gr. 820, .	41·0	39·5	35·8	44·2
Lubricating oil, ...	39·4	38·4	43·7	45·7
Paraffin, ...	2·0	3·0	3·0	2·7
Coke, ...	2·1	2·7	3·2	2·2
Loss, ...	·8	1·2	1·8	·9
	100·0	100·0	100·0	100·0

This oil, from the wells of the Tarentum Oil, Salt, & Coal Co., yields on distillation 5 per cent. naphtha and 90 per cent. lamp oil. The New York Produce Exchange has decided, for commercial purposes, that by the term "crude petroleum" is to be understood pure natural oil, neither steamed nor treated, and free from water, sediment, or any adulteration; and of a gravity of 44° to 48° Beaumé (·800 to ·782 specific gravity). In general the New York crude oil is of a specific gravity varying from ·790 to ·800 (A. Bourgougnon, *American Chemist*, September 26, 1876).

About one-sixth of the whole American produce of crude oil is refined in New York; and in all commercial transactions this oil has to be analyzed, the inspectors being licensed for this purpose by the New York Produce Exchange. Generally the inspectors examine the density and odour, and how the oil feels with the fingers, and make a fractional distillation in tenth parts, giving a report stating that the oil does not contain more than 17 per cent. of naphtha.

The expansion of this oil, both crude and refined, is very considerable, its co-efficient varying from 0·00082 to 0·00086 per degree Centigrade. The variation is according to the amount of naphtha contained in the oil. A knowledge of this is important, as otherwise the barrels filled too full may burst from the expansion consequent upon the rise of temperature on shipboard or during storage. A space amounting to nearly 2 gallons should be left in each 40-gallon barrel; this would allow for a rise of 50° C. in temperature.

Bourgougnon, one of the inspectors, has rejected this system of distilling in tenths, as it does not show the exact proportion of naphtha in the oil; and this is important, since the crude oil is taxed in some countries according to the proportion of this ingredient. He makes the distillations in one hundredth parts, and states that this is the only way to obtain the real percentage of naphtha, benzine, burning oil, &c. The following analysis made by him on this plan shows the average composition of the crude petroleum of the New York market:—

DISTILLATION.

Per Cent.	Gravity.	Beaumé.	Per Cent.	Gravity.	Beaumé.	Per Cent.	Gravity.	Beaumé.	Per Cent.	Gravity.	Beaumé.
1	0·679	78·0	26	0·737	61·3	51	0·778	51·0	76	0·825	40·3
2	0·680	77·7	27	0·742	60·0	52	0·780	50·6	77	0·826	40·1
3	0·685	76·2	28	0·746	59·0	53	0·781	50·3	78	0·827	39·9
4	0·690	74·6	29	0·749	58·2	54	0·782	50·1	79	0·828	39·7
5	0·693	73·7	30	0·750	58·0	55	0·783	49·9	80	0·829	39·7
6	0·695	73·1	31	0·751	57·7	56	0·784	49·6	81	0·830	39·4
7	0·698	72·3	32	0·753	57·2	57	0·785	49·4	82	0·830	39·4
8	0·700	71·7	33	0·754	56·9	58	0·786	49·2	83	0·829	39·7
9	0·703	70·8	34	0·755	56·7	59	0·788	48·7	84	0·827	40·1
10	0·705	70·2	35	0·756	56·4	60	0·790	48·2	85	0·826	40·3
11	0·707	69·6	36	0·758	55·9	61	0·792	47·8	86	0·825	40·5
12	0·709	69·1	37	0·760	55·4	62	0·794	47·3	87	0·823	40·9
13	0·711	68·5	38	0·761	55·2	63	0·796	46·9	88	0·825	40·5
14	0·712	68·2	39	0·763	54·7	64	0·798	46·4	89	0·824	40·7
15	0·714	67·7	40	0·765	54·2	65	0·800	46·0	90	0·825	40·5
16	0·717	66·8	41	0·766	53·9	66	0·804	45·1	91		
17	0·719	66·2	42	0·768	53·5	67	0·806	44·6	92		
18	0·721	65·7	43	0·769	53·2	68	0·808	44·2	93		
19	0·723	65·1	44	0·770	53·0	69	0·810	43·7	94		
20	0·728	63·8	45	0·771	52·7	70	0·815	42·6	95	Residuum or	
21	0·730	63·2	46	0·772	52·5	71	0·817	42·2	96	loss.	
22	0·732	62·7	47	0·773	52·2	72	0·819	41·8	97		
23	0·734	62·1	48	0·775	51·8	73	0·821	41·3	98		
24	0·735	61·7	49	0·776	51·5	74	0·823	40·9	99		
25	0·736	61·6	50	0·777	51·3	75	0·825	40·5	100		

The composition of the crude oil furnished by the above distillation is as follows:—

Naphtha, ...	0·700	specific gravity,	17 per cent.
Benzine, ...	0·730	" "	9 "
Burning oil, ...	0·783	" "	64 "
Residuum—loss, ...			10 "

The specific gravity of the crude oil was 0·7982 at 15° C. (59° Fahr.)

The crude oil very often does not contain so much naphtha; but generally, according to Bourgougnon, New York oil will furnish—

12 to 15 per cent.	naphtha at	0·700	specific gravity.
9 to 12 "	benzine at	0·730	" "
and about 60 "	burning oil at	0·795	" "

The residuum contains about 2½ per cent. (calculated on the oil) of dry paraffin.

As has been stated, much gas usually accompanies petroleum, often causing its free flow, and always

escaping from it when it has been put into the tank to settle. These gases have been analyzed by Professor Henry Wurtz,* and more recently by Samuel P. Sadtler.† Their results are appended in a tabular form :—

	Well in West Bloomfield, N.Y. Wurts.	Burns' Well Gas. Sadtler.	Leechburg Gas. Sadtler.	Harvey Well Gas. Sadtler.	Cherry Tree Gas. Sadtler.
Carbonic acid,.....	10·11	·34	·35	·63	2·28
Carbonic oxide,.....	—	trace	·26	trace	—
Illuminating hydrocarbons of $C^{n}H_{2n}$,	2·94	—	·56	—	—
Hydrogen,.....	—	6·10	4·79	13·50	22·50
Marsh gas,.....	82·41	75·44	89·65	80 11	60·27
Ethyl hydride,.....	—	18·12	4·39	5·72	6·80
Propyl hydride,.....	—	trace	trace	trace	—
Oxygen,.....	·23	—	—	—	·83
Nitrogen,.....	4·31	—	—	—	7·32
	100·00	100·00	100·00	99·99	100·00

Petroleum Refining.—The crude petroleum is but seldom fit for any of the purposes for which its various products are utilized, and therefore its preparation for subsequent employment has given rise to the comparatively new industry of petroleum refining. The immediate object of the refiner is to separate from the natural oil—1st, those lighter hydrocarbons which, by their easy inflammability, would render the oil dangerous; 2nd, those heavier constituents which are more useful as lubricating oil, and which contain paraffin in solution; 3rd, to deprive it of colouring matters, foreign substances communicating to the oil an unpleasant odour, and tarry matters, which otherwise would incrust the wick. The means employed are usually three.

Fractional distillation enables the refiner to effect the first two objects; whilst by treatment with acid and alkali of the liquid from which both the heavier and lighter constituents have been removed, it is rendered fit for use as an illuminating agent.

This refining is but seldom carried on near the wells; more often the natural product is conveyed in round wooden tanks by rail (one or two tanks occupying a car) to one of the great refining centres, of which Cleveland, New York, Baltimore, and Pittsburg are the principal.

This transport by means of railway cars has in some cases been replaced by a system of pipes. A company was formed some years ago in Pennsylvania to convey the oil from the wells to the seaports on the Atlantic. This company now intends to construct a tube of 4 inches diameter and of some 300 miles in length, connecting the wells with the sea. The practical possibility of the plan is proved by works which, for a distance of 250 miles, are already in use. Baltimore was the first city with which these new canals were connected. The oil is forced through the pipes at a pressure of 900 lbs. on the square inch; and at intervals of 15 miles large steam pumps, of 10-horse power, assist the motion of the stream. At Baltimore the canal ends in enormous tanks, and these are in direct communication with the refining tanks. The cost of the new canal and accessories is calculated at 1,250,000 dollars.

As in many minor details the methods adopted by different firms vary considerably, we shall supplement a *resumé* of the more important features of the process, first, by a more detailed account of the varieties of plant employed, and then by the abstract of an account furnished by the late Professor E. Parrish, of Philadelphia, of the *modus operandi* at the Franklin Oil Works, near that city.

From the wooden tanks we have mentioned the oil is pumped into large underground reservoirs, in which it is allowed to stand, so that any sand or the heavy impurities may sink. From these it is transferred either into what are called the "naphtha stills" (large wrought-iron stills or upright cylinders of a capacity of 12,000 gallons each), in which by simple steam heat some 15 per cent. of the lighter constituents, collectively termed naphtha, is separated; or more usually into stills of wrought iron inclosed in brickwork, capable of holding variously from 1000 to 140,000 gallons. That in Plate "Petroleum" holds a charge of 19,000 gallons, and is heated by eight fires underneath. These stills are heated by fires, the residual "coke" of previous operations generally furnishing the fuel. The still is connected with a condenser, a wrought-iron pipe submerged in water or ice, according to circumstances. Sufficient heat having been applied to cause the oil to boil, the more volatile compounds speedily begin to come over. The lightest of these are sometimes allowed to escape, more often utilized as fuel, as at the works we more particularly describe; and sometimes collected, either by surrounding the condenser with ice, or by compressing the vapours with a powerful air-pump in a very strong receiver. The very volatile liquids known as rhigolene and cymogene are thus obtained.

Immediately succeeding these the lighter portions, which may be condensed at the usual atmospheric temperature, begin to appear. The oils first obtained have a specific gravity of about ·630 at 60° Fahr., the product gradually becoming heavier as distillation proceeds. When it is of specific gravity varying with different refiners from ·725 to ·750, the stream is diverted from the naphtha tank into which it has been flowing into the kerosene receiver, where it is collected until its gravity reaches about ·840; after which its direction is again changed, and the paraffin oil tank receives it till there is nothing further to come off. The last products have a specific gravity of about ·907. The residue in the still, usually, though improperly, termed coke, is largely composed of earthy matters and carbon, and though by itself nearly incombustible, may be utilized for fuel by admixture with bituminous coal.

The crude naphtha is subsequently separated by distillation into three products—gasoline, the lightest, next naphtha, and finally benzine. When steam is employed in the first instance, four products are

* Silliman's Journal (2), xlix. p. 336.
† American Chemist, September, 1876, p. 98.

usually obtained, called respectively gasoline, A, B, and C naphtha, the first of which is often redistilled for rhigolene.

In some cases, however, when burning oil is the sole object, this crude naphtha is sold to well proprietors, who pour it down the wells, nominally to clean them, but practically to sell it once more as "crude oil" to the refiners. Frequently, too, the dishonest practice of pouring it directly into the "crude oil tank" is resorted to. According to Dr. C. F. Chandler this adulteration averages 15 per cent.*

The crude "kerosene" (an American generic term for the burning oil, whether crude or refined), is then mixed in a suitable vessel with sulphuric acid and thoroughly agitated, so as to remove both the odour and colour which it still has. The proportion of oil of vitriol is about 2 per cent. by volume. The mixing is effected either by revolving stirrers or by forcing atmospheric air rapidly through the liquid. After standing till the dark tarry sediment which formed has subsided, the clear oil is drawn off and agitated with water; then with solution of alkali, soda, or ammonia; and finally, this is thoroughly washed by more water, leaving the oil "sweet." A few firms submit the product to a final distillation; but most of the commercial oil is sold without further purifying. It is very important to completely wash out the chemical agents employed, as otherwise the oil deteriorates in value with age, through acquiring more or less colour.

In many cases the point at which to divert the stream into the paraffin oil tank is determined by the colour of the distillate, it being allowed to run into the kerosene tank no longer than it continues to run "light," or whiter still, of a "light straw" tint.

The distillation is sometimes continued, as we have said, till nothing more can be obtained. At other works it is stopped as soon as the "residuum" reaches the consistency of very thick oil or fluid tar; this is generally the case when very large stills are employed. The distillate, crude lubricating oil, requires more careful treatment than either of the preceding products. According to S. Dana Hayes,† it is first agitated with sulphuric acid and then distilled with caustic soda, the product being mostly dense paraffin oil. This is placed in wooden barrels in icehouses, where it remains for from seven to ten days; and during this time the paraffin wax crystallizes, so that the masses retain the form of the barrels when they are removed. It is now put into bags made of strong cloth, which are arranged one above another, with sheets of iron between them; and when submitted to heavy pressure it yields crude scale paraffin wax remaining in the bags, and heavy oil pressed out. The crude paraffin is refined by repeated solution in naphtha, recrystallizing, and pressing, until it is perfectly white and pure, ready for sale.

In some establishments neither the lightest nor the heaviest constituents of petroleum are separately obtained, the natural oil being resolved into three products only, viz., 1, crude naphtha; 2, burning oil; 3, residuum. The operation by which the heavier hydrocarbons are converted into burning oil, technically known as "cracking," was accidentally discovered by Mr. Joshua Merrill, one of the great promoters of the coal oil refining in America, who was annoyed by finding that the heavier oils, from which he was endeavouring to obtain lubricating oil by distillation, invariably split up into lighter hydrocarbons which were useless for his purpose. In trying to ascertain conditions by which this could be prevented, he found that "a continuous production of light distillates having a specific gravity of ·818 was effected from hydrocarbon oils of specific gravity ·880, in an apparatus holding 1000 gallons, by properly regulating the heat applied; the other products being only uncondensed gases and deposited carbon, left in the apparatus at the end of the distillation."*

The very last distillates obtained from all the products are heavy, dark-coloured liquids, known as "cokings." They are mixed and generally distilled when a sufficient quantity has accumulated, yielding crude lubricating oil. The residuum of most of the operations consists of carbon mainly, with which much of the soda employed will remain; it is therefore burned in a suitably constructed fireplace, and the alkali, now carbonate, is obtained by lixiviating the ashes.

The black acid liquid containing the oil of vitriol employed, technically termed "sludge," is generally sold to manure-makers for the manufacture of superphosphate.

With regard to the stills employed in petroleum refining, no settled form is universally employed. Generally they are made of cast iron, though wrought-iron stills are probably most economical; cast iron, if cooled suddenly, being so liable to fracture, a current of air from an open furnace door will often cause the bottoms to crack (Gesner). In such case the mode of repairing is by a plate of boiler iron being bolted over the fracture. Stills made of boiler plate have been tried; but when a high heat is required and they are exposed to the direct action of the fire they are soon destroyed, or commence leaking at the rivets. When the heat exceeds 560° Fahr., which is necessary in the distillation of the heavier oils and paraffin, they are in danger, unless they are protected by the admission of steam, and guarded against the fire of the furnace. Whether the still be of cast or sheet iron, it is always unsafe to run the oil down so as to "coke" the bottom.

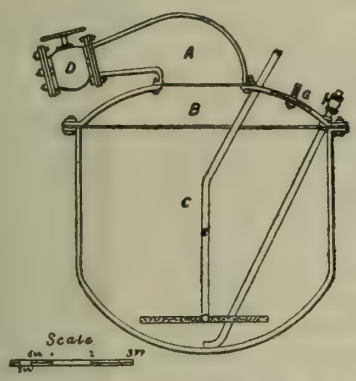
Gesner is of opinion that the largest stills employed for distilling the crude oils as they come from the retorts or oil springs, should not have a greater capacity than 1600 gallons. The diameter may be 8½ feet and height 4½. The crown should be moderately concave upwards to the neck. In the cut adjoining (Fig. 17) a valve is represented upon the goose neck at D. This has been used to blow out the

* American Chemist, vol. ii. 12, 447.
† Amer. Chemist, vol. ii. No. 11, p. 405.

* American Chemist, ii. 11, 402.

tarry contents of the still by the pipe F, by admitting steam by the pipe E, closing valve D, and opening the valve or pipe F. A, gooseneck; B, dome; C, kettle; and G, manhole. When the still bottoms are

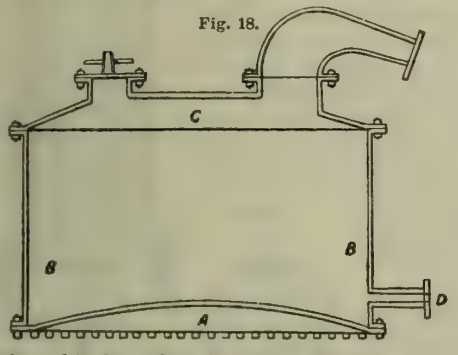
Fig. 17.



made convex, however, the ordinary pipe and cock can be used to draw off the residuum. The draw-off pipe may be of wrought iron of 2 inches diameter, inserted into the side of the still by a screw, and secured on its inner end by a lock nut.

When high temperatures are required so as to distil various oils to a pitch or coke, the still shown in Fig. 18 may be employed. The bottom, A, is 2 inches

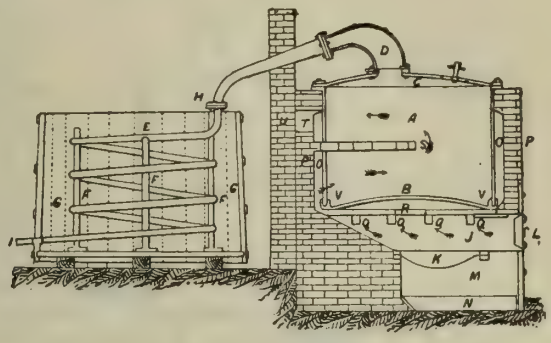
Fig. 18.



thick, and is flanged to the side, B, with three-quarter inch bolts 6 inches apart. The sides are flanged to the dome or cover, C, in the same way. The sides form a cylinder when cast, and the outlet pipe, D, 3 inches in diameter and 1 foot long, is cast with it. This still, 7 feet in diameter and 4 feet deep, has been used in distilling both candle tar and coal tar. In both cases the distillation was carried on until a coke remained, and the heat was such as to maintain the still bottom in a state of bright redness. The bottom was burned through every two months, and a new one bolted to the sides.

Such a still, in connection with its worm or condenser, is shown in section in Fig. 19. This still is a cylinder of cast iron, 7 feet in diameter and 1 inch in thickness, sitting in a groove, V, which is carried around the bottom, B. This bottom is 1½ inch thick. The dome, C, is low, not rising more than 1 foot 5 inches above the level of the top of the side. The goose-neck, D, is three-quarters of an inch thick, 1 foot 3 inches wide where it is fastened to the dome, and tapering down to 8 inches where it joins the

Fig. 19.



pipe which connects it with the worm, E. The pipe connecting the goose-neck and worm tapers from 8 to 4 inches where it joins the worm, E. The worm is a spiral coil of wrought-iron pipe, fastened securely by iron stays, F, into the worm tank, G. The worm coil contains 100 feet of pipe, tapering from 4 inches in diameter at H to 2½ inches at the tail pipe, I. It is made by joining equal lengths of 4-inch, 3-inch, and 2½-inch pipe. Where the tail pipe passes through the worm tank, it is secured, and leakage round the pipe prevented, by two lock-nuts, one on each side of the stave, a thread of sufficient length having been cut on the pipe to allow the lock-nuts to be applied.

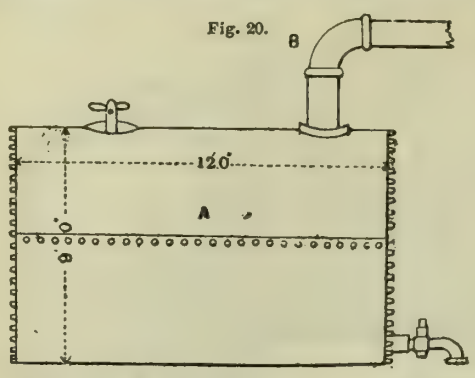
The worm tank is made 7½ feet in diameter and 6 feet deep; made of 3-inch staves, and bottom, and hooped with four hoops, 3 inches wide and three-quarters of an inch thick.

The still is heated by the furnace, J, when open fire is used. The fire bars, K, are 4 feet in length, and cover 1 foot 6 inches in width. The furnace door, L, is 1 foot 4 inches high, and 1 foot 3 inches wide. The ash-pit, M, corresponds with it in size. The water pan, N, corresponds with the ash-pit in width, and is 6 inches deep. The length of the ash-pit and pan is the same as that of the furnace bars. The space, O, round the still is 4 inches wide, and the walls, P, one brick thick. The throttles, Q, are 8 inches deep and 4 inches wide. They are small flues which distribute the heat round the still. The still bottom rests upon the fire-tiles, R, which cover the throttle, and are laid in a circle. The bridge, S, prevents the heat from escaping at once by the flue, T, to the chimney, and brings it forward around the front of the still. The wall, U, is the division wall between the still-house and the refinery.

The still commonly employed (Gesner) by the American petroleum refiners is shown in Fig. 20. It is a cylinder of boiler iron, A, 12 feet long and 9 feet in diameter. Its working contents are 80 barrels, or 3200 gallons. The goose-neck, B, is a 4-inch elbow, connected with a 4-inch wrought-iron pipe. The draw-off cock is at the bottom end, furthest from the fire, which is applied much in the same way as to a steam boiler. The plates are 12-inch

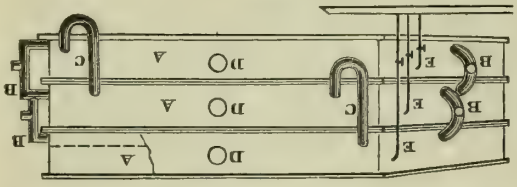
lengths, and present no rivetted seams to the action of the fire.

Fig. 20.



Messrs. E. F. Prentiss & Co., of Birkenhead, have patented a "continuous still" (Fig. 21), for the cut and description of which we are indebted to Norman Tate. A A A are three stills, placed one

Fig. 21.



above another. Each still consists of a steam chest and a chamber for containing the oil to be distilled. The division between the steam chest and the oil chamber may be seen in the top still. B B B show the position of the steam cocks and pipes, by means of which steam is introduced into the still; C C are syphon pipes, for conveying oil from the upper to the lower still; D D D are pipes for the escape of vapour; E E E are pipes for carrying away the water which condenses in the steam chambers.

The three stills are kept at different temperatures. The first is kept at a temperature sufficiently high to drive away the spirit; the second is kept at a temperature high enough to distil the burning oil; the third is kept at a temperature sufficient to distil all the heavier portion of the oil.

In the highest still all the oil which is not converted into vapour by the temperature at which the still is kept passes by means of the syphon tube, C, into the still next below it; and then, owing to the temperature being higher, a portion of it is converted into vapour, and distils over. There is, however, some of the oil yet remaining, and this requires a little higher temperature for its distillation. It is therefore conveyed by the syphon, C, into the lowest still, and there distilled. Only a thin layer of oil is kept in each still, so that evaporation proceeds very rapidly. Since this still has been in use, hot air has been found a more suitable heating agent than steam.

Connected with this still is a condensing apparatus (Fig. 22), the invention of the same firm, so arranged as to collect separately the different products of the distillation. A is the entrance from the still, the arrows showing the course taken by the vapours until their exit at B, from whence they proceed to the next column. The bottom of the column is divided by a cast-iron partition, C, made tight to the plate, D, which supports the tubes. The position of the tube is shown in section (Fig. 23). E is a copper case for the application of steam to heat the contents of the column; F is a copper vessel to contain the air, the action of which helps to regulate the heat of the column; G shows an arrangement for admitting cold liquor to cool the contents of the column when required; H is an overflow; I is a steam pipe for keeping that part of the column warm; J J are exit pipes for the condensed liquors. Three or four such columns are connected with each still, each column being kept at a different temperature to the others, the heat being so arranged that the product may be condensed and collected separately in the column set apart for the purpose (Norman Tate, "Petroleum and its Products," p. 76).

Fig. 22.

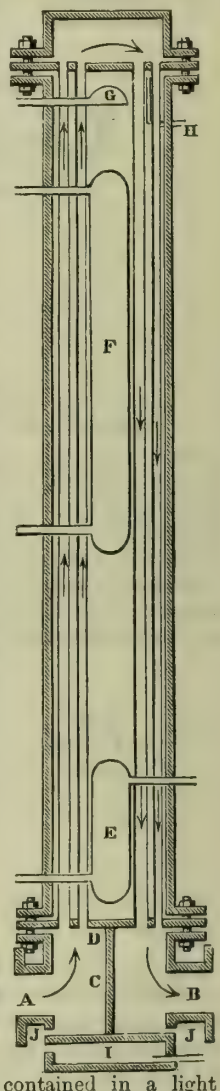


Fig. 23.



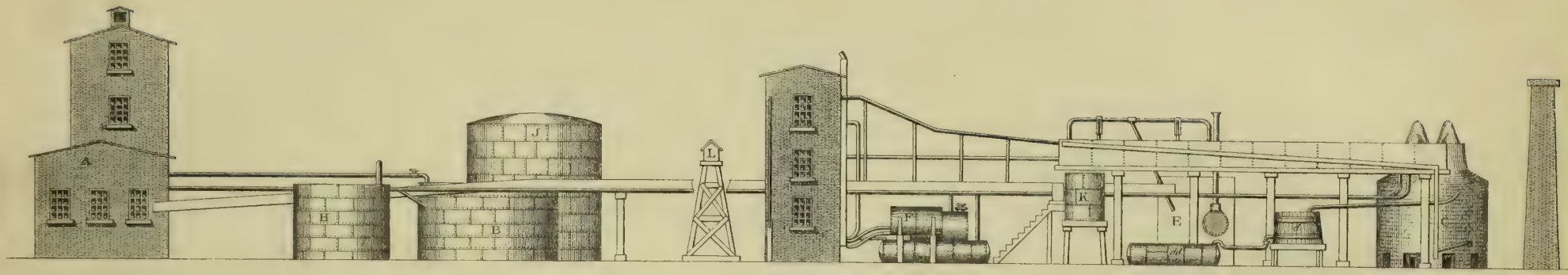
The most practical condensing arrangement is that of several tiers of cast-iron pipes, contained in a light malleable-iron tank, through which the water is allowed to circulate; the turning in the pipes being effected by means of snail bends. When the heavier oils which contain much paraffin are being condensed, it is necessary to keep the water at 70° to 80° Fahr., to prevent the paraffin from solidifying and obstructing the passage.

The washers or agitators may be either vertical or horizontal. The vertical washer is of light boiler iron, having a concave bottom to assist the drawing off of the tarry matter thrown down by these reagents. A shaft with fans of wood or iron, placed obliquely as in a ship's screw, is turned by gearing. Breaks of wood 6 inches wide and 1 inch thick are secured to the side. These serve to break the current produced by the fans, and make the agitation more thorough. The bottom should be surrounded

PETROLEUM.

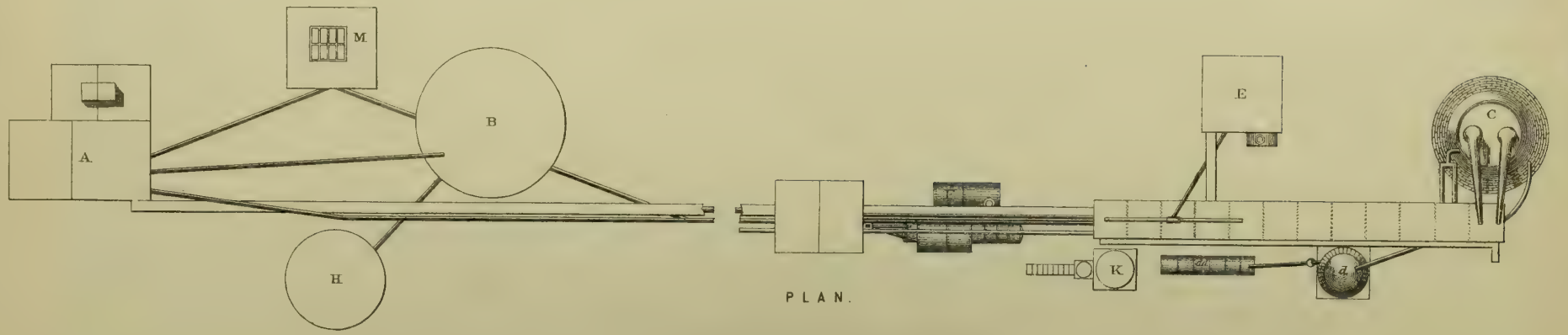
FRANKLIN OIL WORKS, PHILADELPHIA.

Plate I.



ELEVATION.

A	*Pump House & Refinery.*	F	*Benzine & Gasoline Receivers & Stills*
B	*Crude Petroleum Tank.*	H	*Receiving Tank.*
C	*Wrought Iron Still.*	J	*Kerosene Tank.*
d	*Worm & Tub.*	K	*Agitator.*
dd	*Iron Receiver.*	L	*Lantern.*
E	*Boiler House.*	M	*Bleaching House.*



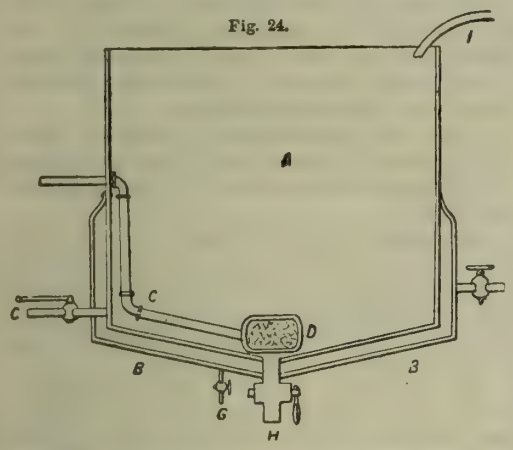
PLAN.

J. B. LIPPINCOTT & CO. PHILADELPHIA.

by a steam jacket, to admit of its being kept at 90° Fahr. when in use.

This washer has the merit of simplicity, and in this respect is better than the horizontal form. For general use, however, the best agitator is the air agitator, Fig. 24. It consists of a vessel of thin

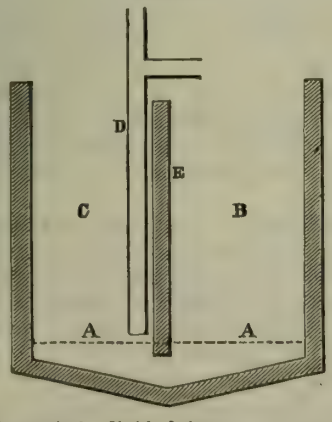
Fig. 24.



boiler iron, A, surrounded at the bottom and part of the sides by a steam jacket, B. A 2-inch wrought iron pipe, C, communicates with a blowing fan, such as are used for small blast furnaces, or with an air-pump. The pipe, C, enters a perforated iron vessel, D, or may be left coiled up with its end open on the bottom of the agitator. This arrangement leaves the interior of the agitator clear of all obstructions. A steam pipe and valve admit steam to the jacket. The drip-cock, G, carries off the condensed steam. The cock, C, is the outlet for the oil after agitation, where a settling vessel is used, or the oil is discharged into another agitator, as in coal-oil refining. The pipe, I, is the inlet from the pump. The cock, H, is for drawing off the acid residuum. The drawing represents an agitator 7 feet in diameter and 6 feet high (Gesner, "Coal Oil," p. 84).

A washer invented by Gouldie, of the Albion Oil Works, Birkenhead, may be described here. A

Fig. 25.



vessel (Fig. 25) is divided into two compartments by means of a partition, E, down the centre; this partition, however, does not quite reach to the bottom. Sulphuric acid is first run into and occupies the bottom of the vessel, up to the point indicated by the dotted line, A. The oil is now run into compartment, B, and as soon as there is a sufficient weight of oil in it is forced through the acid, and rises into the other compartment, C, from which it is pumped back again by means of the pump, D; and the process goes on in this way until the oil has been sufficiently treated (Norman Tate, "Petroleum and its Products," p. 73).

When agitating with soda solution it is preferable to use manual labour, stirring it with a rake or plunger, as the use of machinery is apt to convert the mixture into a jelly like substance, thus spoiling the product. The hand stirring, when carefully performed, effectually robs the oil of all acid traces.

The operations of petroleum refining are conducted in the Franklin Oil Works, Philadelphia, as follows:—"In the frame building, A (see Plate I.), are four pumps worked by steam—one for pumping water, one crude petroleum, one kerosene, and one for forcing a powerful current of air into the rectifier, and into pipes communicating with the several reservoirs and the still. By these pumps the crude oil is transferred from the receiving tank to that marked B, thence, as required, to the still; and the main portion of the distillate is sent to the rectifier, thence to the bleaching-house, and thence to the large tank, J, all without labour, loss by evaporation, or danger from fire. The still, C, wrought iron with a steel bottom, of 19,000 gallons capacity, is situate at the southern end of the inclosure. It is inclosed by brickwork in which are eight furnaces; this reaches to within about 6 feet of the top, which is somewhat drum-shaped, and has two necks, through which the vapour is conveyed to the cooler.

Besides these, which carry off the more volatile vapours, there is a pipe inserted lower down in the still, which conducts the heavy lubricating and paraffin oils coming over towards the end of the process, through the worm and tub, *d*, to an iron receiver, *d d*. To aid in collecting these least volatile products, which are for the most part condensed in the top of the still, a ledge extends round the inside, just at the point of insertion of this pipe.

The main cooler consists of several courses of iron pipe, running horizontally through a closed wooden trough 80 feet long, into which a stream of cold water is conveyed by a pipe, shown in the drawing, from near the top of the adjacent building, in the basement of which there is a pump for its supply. The inclination of this water-pipe causes it to empty itself whenever the pump ceases to act, thus preventing its bursting, when out of use, by freezing. Surmounting the cooler, several small vertical pipes arise from the lower line of the horizontal condensing pipes for the escape of non-condensable vapour which passes off, especially near the beginning and close of the operation.

As this heavy vapour, when allowed to escape, is a waste material and a frequent cause of conflagration, it is desirable to collect and utilize it; for which

purpose, over the open end of each of the vertical pipes a pipe of larger bore is set, and these are connected with a main which is led into the adjacent boiler-house, E, where a jet of steam is discharged into it in the direction of the fire-box, a draught being thus created by which the highly inflammable vapour is carried under the boiler, and by its combustion made to aid in generating the steam required for working the pumps.

The pipe which conveys the steam to the distant pumps is inclosed in an elevated wooden trough, filled with sawdust to prevent condensation; and this is also used for the support of the pipes connecting the air pump with the reservoirs and still. The other pipes, used for the conveyance of petroleum, are laid on the surface of the ground, where any leakage may be easily discovered. The tall frame building to the left of the terminus of the main cooler is appropriated, on the lower floor, to a pump, as before stated; on the second floor, to the separator, which is a cast-iron box open for the reception of the distillate, and connected through the bottom with pipes leading to the receivers for benzine and kerosene, respectively. Here these liquids are tested by their specific gravities, and separated previous to undergoing further treatment.

The benzine and gasoline receivers and stills are located near this building on either side. One is shown in the Plate, marked F. A steam pipe passes into this still, and the still communicates, by another pipe, with a refrigerated coil in the third story of the above-mentioned building. This coil is constructed with a view to separate the distillate to be sold as gasoline from that to be sold as benzine.

A pipe leaves the coil midway, through which the more easily condensable portion of the mixed product is collected (the worm above this being surrounded with water at 80° Fahr., and below with water not above 60° Fahr.), while the gasoline, which is only condensed by passing through the entire length of the coil, is delivered into an appropriate receiver, mostly underground, and covered by a shed.

Following the line of pipe from the separator, and passing the crude petroleum tank, B, we come to the receiving tank for the great body of the distillate, H. The portion designed for kerosene being received here is transferred to the refinery in the upper part of the building, A. This consists of an open wrought-iron boiler lined with lead, in which 225 barrels (of 44 gallons each) of the distillate are agitated with 10 carboys of sulphuric acid, by means of atmospheric air forced in at the bottom. A strong odour of sulphurous acid is given off during the ebullition, and the kerosene is found to have lost an objectionable adhesive property, and to be less liable to "gum."

By subsequent continued agitation with water, and lastly with soda, the acid is removed. The air-pump now being shut off, the oil rises to the surface, and is drawn off to the bleaching house, which is a large shed, M, shown in the ground plan, having a roof partially of glass, and covering an open tank about 25 feet in diameter. Here the kerosene is exposed to the sun's rays, and to a temperature somewhat above 110° Fahr., produced by a steam pipe, which is protected from direct contact with it by a 3-inch cast-iron pipe in which it is inserted. The effect of 10,000 gallons of this brilliant liquid with the sun shining directly upon it is most striking; the refraction of the light gives to the bottom of the tank the appearance of a constantly changing concavity, with the greatest apparent depth nearest the point of observation. The opalescence or fluorescence is superb.

From the bleaching-house the kerosene is forced by the appropriate pump from the tank, J (not shown in the ground plan), whence it is drawn for barrelling.

An ingenious automatic faucet is used for filling the barrels; this being inserted tightly into the bung the escape of air is through it, and as soon as this ceases, from the barrel being full, a leather diaphragm subsides and releases a cut off held by a cord, so that the flow of liquid stops.

The agitator, K, receives the refuse and any portions of the distillate unsuited to go into either of the finished products, that it may be mixed and prepared to be returned to the still. The lantern, L, is elevated so as to be removed from escaped vapours: when lighted it throws a strong light into the separator, a part of the apparatus which it is very necessary to inspect and adjust at night, as well as by daylight.

Twice a week a charge of the crude oil is forced into the still. The fires are then kindled, water turned on in the main cooler, the jet turned into the gas-pipe communicating with the fires under the boiler, and the pipes connected with the separator arranged to collect the parts of the distillate designed to be converted by fractional distillation into benzine and gasoline.

During the early part of the process the specific gravity of the condensed material is taken from time to time at the separator; and when it reaches 85° Beaumé (specific gravity ·661), the pipe communicating with the gasoline receiver is closed, and it runs into the benzine receiver until it reaches 66° B. (specific gravity ·720), after which it passes on to the larger distillate receiver. Sometimes the heavier portions of the benzine are returned to the still, and thus become mixed with the kerosene distillate in a subsequent part of the process; and if there is no market for gasoline, this may also be returned, and may add to the uncondensed vapour consumed under the boiler, and perhaps to the available condensed products.

According to B. J. Crew, who has had experience in this process, crude petroleum gives off uncondensable vapour from 60° Fahr. to 160° Fahr.; from 160° to 280°, the benzine or naphtha comes over; from 280 to 600°, the oil suitable for illumination; and above 600°, paraffin oil.

Petroleum Products.—The proportion of the various products obtained at the Franklin Oil Works is approximately as follows:—Gasoline, 8 per cent.; benzine or naphtha, 12 per cent.; paraffin or lubri-

cating oil, 5 per cent., and the remainder is kerosene. The fixed residuum varies in quantity and consistence with the persistence of the operation and the quantity of crude oil; from one charge of 19,000 gallons, an average of about 6½ barrels is obtained.

The accompanying table, abridged from Dr. C. F. Chandler's report * to the Health Department, New York city, will show the percentage, &c., of the different products obtained from crude oil by destructive distillation :—

PRODUCTS OF THE DISTILLATION OF CRUDE PETROLEUM.

Price in Bulk, 14 *cents per Gallon.*

Name.	Percentage Yielded.	Specific Gravity.	Mode of Condensation, Uses, Synonyms, &c.
Cymogene,	—	·590	Condensed by pump; made by one firm only for an ice machine; boils at 32° Fahr.
Rhigolene,	—	·625	Condensed by ice and salt; used as an anæsthetic; boils at 65° Fahr.
Gasoline,	1·5	·650 to ·665	Condensed in worm by cold water; used in "air gas machines" and "gas carbonizers."
Naphtha,	10	·695 to ·705	For oil cloths, cleaning, &c.; so-called "safety oil," "Danforth's oil," "American safety gas," &c.; for adulterating kerosene, cleaning oil wells, &c.
Benzine,	4	·725 to ·737	For varnishes and paints.
Kerosene or refined petroleum,	55	·802	Ordinary oil for lamps.
Paraffin oil,	19·5	·880	Semi-solid when cold; chilled and pressed to separate paraffin; oil used for lubricating.
Coke, gas, and loss,	10	—	

The paraffin would probably amount to ·2 per cent. of the natural oil. The above table must not be considered as applying to all samples, but only as an average yield for Pennsylvanian petroleum of about ·807 specific gravity. By cracking, the same oil would yield—

	Per Cent.
Crude naphtha,	20
Burning oil,	60
Coke and loss,	14
	100

Of these products a few call for a more extended notice.

Rhigolene.—This very volatile liquid, a discovery of Joshua Merrill, made in 1866, was at that time considered the lightest of the petroleum hydrocarbons. According to S. Dana Hayes, it was made at the instigation of a Boston surgeon of note, Dr. Henry J. Bigelow, who wanted to try if such an agent could be used to produce local anæsthesia, as ether is still constantly used, during short surgical operations. Its use was attended with success, and many hundred gallons have since been thus employed. It boils at 65° Fahr., has a specific gravity of ·625, and evaporates so rapidly as to depress the mercury in a Fahrenheit thermometer in twenty seconds to 19° below zero.

Benzine, known also as "petroleum spirit" and "turpentine substitute," is a colourless, highly volatile liquid, with usually a pleasant ethereal odour. Gravity, ·720 to ·740. It is, of course, very inflammable. It would appear to be a very good substitute for turpentine; paint made with it flowing more freely from the brush, drying more quickly, and being free from objectionable odour. The best samples as they evaporate leave a deposit as a shining bituminous varnish, which both adds to the beauty of the paint and serves as a protection. On the other hand, "benzine" sometimes contains sulphur, which, forming black sulphide of lead, communicates a brownish tint when this liquid is used for lightish-coloured paints. Also, if the sample employed be a very light one, its great volatility will cause the paint to dry almost before it leaves the brush.

A good sample of petroleum spirit should leave no permanent stain on paper on which it has been dropped. The best specimens for paint purposes have a specific gravity of from ·725 to ·735 (Norman Tate).

This distillate is also successfully used for dissolving india-rubber, &c., for water-proof materials; also for removing grease spots from dresses, &c. It can never come into the general employment that it merits until its composition is uniform, which at present is far from being the case.

So called "mineral sperm" oil is an interesting instance of the application of the cracking operation. It is a heavy oil (specific gravity usually about ·850), and is so far from being a volatile oil, that it will not burn unless raised to a temperature of 300° Fahr., nor does it give off an inflammable vapour at any lower temperature than 262° Fahr. Its great safety may be seen by the fact, that the flame of a ball of yarn saturated with oil and ignited, is immediately extinguished by being plunged beneath the surface of this oil, even when it has been heated to 200° Fahr.* It is made from heavy paraffin oil, which is "passed through a partially destructive distillation, cracking it enough to lessen its viscidity, but not enough to render it volatile; its increased mobility causing it to ascend the wicks freely, whilst it still preserves its character as a fixed oil." The high appreciation of its qualities may be gathered from the fact, that in 1871 the quantity manufactured was estimated by its discoverer, J. Merrill, who patented the process both in America and Great Britain, as being a quarter of the whole petroleum production, or 160,000 gallons daily.

To the enterprise and ingenuity of this gentleman is owing another important petroleum product, which is valued on account of its lubricating properties, viz., "neutral heavy lubricating oil." When

* Amer. Chem. ii. 12, p. 446.

* Amer. Chem. ii. 11, 404.

in consequence of the discovery of petroleum the coal oil industry began to be to a great extent abandoned, the supply of material for the manufacture of heavy lubricating oil became very small, and recourse was had to the heavy paraffin oil, which was more frequently sold by most makers of burning oil than rectified. The objection, however, which for a long time attended its use, was the offensive odour and unsightly appearance of the products. In November, 1867, as the result of an accident, a method was discovered of obtaining an oil suitable in all respects for lubricating, and perfectly unobjectionable in the particulars we have mentioned.

The distillation of 900 gallons of this heavy paraffin oil was being proceeded with at the South Boston Works, under J. Merrill's management, when it was found that, owing to some partial stoppage in the condenser, the presence of vapour was forcing some of the oil through the joints at the bottom of the still, whence it oozed into the fire beneath. As the matter appeared to increase, an attempt was made to empty the still by very slow distillation; this was, after some 250 gallons had passed into the receiver, abandoned, and the fire gradually withdrawn. On the next day, on removing the oil left in the still, it was found to be clear, odourless, neutral, and dense. It was discovered thus that by slow heat and its gradual removal all the lighter hydrocarbons which conferred the odour might, without decomposition, be separated, leaving merely the heavy oils with which they had been mixed. Subsequently the means for the removal of the odorous bodies were perfected by introducing steam into the body of the oil in the still, which greatly facilitates the escape of the lighter constituents. So great is the demand for this product, that, in 1871, 50,000 gallons of this oil were imported into England for lubricating machinery.

As has been indicated, the safety of a given specimen of petroleum is not dependent upon its specific gravity, but upon the temperature at which it gives off an inflammable vapour, in other words, upon "its flashing point;" and there can be no doubt that the amount of unsafe oil annually sent from the refineries is mostly to be laid to the charge of the refiners, who, because there is no sufficient market for naphtha, do not allow the distillate to run into the naphtha tank until all those hydrocarbons which would render the oil unsafe have passed over, but transfer it prematurely into that for crude burning oil. Dr. Chandler speaking on the subject says—"On every gallon of naphtha run into the kerosene tank there is a profit to the refiner of 20 cents (10*d.*), or on every per cent. of naphtha added to the kerosene a reduction of one-fifth per gallon of the cost of production, which, with kerosene at 25 cents (1*s.* ½*d.*) per gallon, amounts to 1¼ per cent. For every gallon of naphtha sold as kerosene, the refiner can afford to throw away 4 gallons. Nothing can be more desirable than the discovery of some use to which the naphtha can be put, which will make such a demand for it as to raise its value above that of kerosene, that it might be the interest of the refiner to separate as much instead of as little as possible."

A safe oil might be made with ease by running off the naphtha till a specific gravity of 58° Beaumé is reached in the distillate, instead of 65° to 62° Beaumé, the usual point, and then exposing the oil in shallow tanks to the sun for a few days; the increased expense in refining would not amount to more than 3 or 4 cents (1½*d.* or 2*d.*) per gallon.

The important influence upon flashing point which a small percentage of naphtha has, is seen by reference to the experiments of Dr. B. W. White, president of the Board of Health of New Orleans, on this subject.

He worked with an oil which flashed at 113° Fahr., and found that an addition of—

		Degrees Fahr.
1	per cent. of naphtha caused it to flash at.....	103
2	" " " "	92
5	" " " "	83
10	" " " "	59
20	" " " "	40

After the addition of 20 per cent. of naphtha, the oil burned at 50° Fahr.

Ordinary kerosene is said to have a gravity of 47° Beaumé, and to flash at 86° Fahr.

The refined product is, when freshly prepared, colourless and nearly odourless, of a specific gravity varying from ·780 to ·825 (Norman Tate). When any considerable bulk is observed by transmitted light, the phenomenon of fluorescence is seen to be very marked, imparting a beautiful azure tint to the liquid.

It mixes in all proportions with strong alcohol, ether, fixed and essential oils, is not miscible with water, but communicates to it its own odour and taste. It dissolves sulphur, phosphorus, iodine, camphor, most resins, wax, and fats, and softens india-rubber into a glairy varnish.

Chemical Composition.—The present state of our knowledge respecting the composition of petroleum, though still imperfect, is an accumulation of the results obtained by many observers, whose labours we will now briefly notice.

As far back as 1788 Winterl examined a thick black variety of petroleum occurring between Peklenicza and Moslowina in Hungary, reporting that he obtained from it by distillation a colourless oil, a yellow oil, and a buttery mass.*

The Galician product was examined in 1791 by Martinovich,† and in 1817 Saussure investigated the petroleum from Amiano.‡ Twelve years later, in 1829, Unverdorben submitted Persian oil to distillation, and concluded that "it consisted of a mixture of several oils, together with a small quantity of a kind of solid fat (paraffin?), resin, and an indifferent coloured substance."§ Results similar to these were obtained subsequently, in 1831, by Christison and

* Crell's Chem. Annal. i. 493 † Ibid. i. 72.
‡ Bibl. Univ. S. et A. iv. 16.
§ Watt's Dict. Chem. vol. iv. p. 383 (from Schweig Journ. 57-243).

GREGORY with "Rangoon tar;"* in 1833, by BLANCHETT and SELL† with Persian oil; by TOROSIWIECZ, about 1836, with the petroleum from Niebylow in Galicia;‡ by KOBELL in the same year, after investigating the properties and nature of the product of Tagern lake in Bavaria.§ PELLETIER and WALTER, also, in 1840, examined the Italian oil,‖ and HESS that from Baku;¶ and even later, URE and MANSFIELD that from the Alfreton Coal Mine, Derbyshire,** without throwing more light upon the subject, substantially corroborating the statement of UNVERDORBEN, that it was a more or less pure solution of bitumen in a varying mixture of liquid hydrocarbons of different densities.

In 1857 Messrs. WARREN DE LA RUE and HUGO MÜLLER published a report of the investigation they had been engaged in of Rangoon tar. They found it to contain 11 to 12 per cent. of solid matter, which they regarded as paraffin; and after unsuccessfully trying to separate the liquid constituents by fractional distillation, they resorted to a mixture of nitric and sulphuric acids as a means of separating some, which would form nitro compounds from the remaining hydrocarbons, which would be unaffected. In this way they succeeded in obtaining evidence of the presence of benzene and its homologues—viz., toluene, xylene, and cumene, though they found these in but small quantity, and indicated the probability of Burmese naphtha containing several radicals or their hydrides, belonging either to the marsh gas or ethylene series.††

EISENSTÜCK examined the Sehnde petroleum (Hanover) in 1858, and stated that it consisted of homologues of ethylene, and a substance which he called petrol, of formula C_8H_{10}.‡‡

UELSMAN, working on the same oil, came to a different conclusion — viz., that the hydrocarbons were not of the olefine or ethylene series, but of the paraffin series—homologous with marsh gas.§§ FREUND and PEBAL, continuing the research on Galician petroleum, found three series present—viz., the olefines, the benzene homologues, and a third, consisting of members homologous with phenol.‖‖

PELOUZE and CAHOURS then took up the subject, and in a series of papers sent to the Royal Academy of Sciences, Paris,¶¶ have contributed more to our knowledge of the matter than any previous investigators. They concluded that Pennsylvanian petroleum —the only kind they examined — contained at least twelve members of the homologous series, of which marsh gas is the first term. They succeeded in isolating these bodies, and showed that the regular succession from C_4H_{10}, butylic hydride, up to $C_{15}H_{32}$, was present in American oil. Shortly after this RONALDS added to those members indicated by PELOUZE and CAHOURS the two (ethylic hydride, C_2H_6, and propylic hydride, C_3H_8), which he obtained from the gas found floating over the surface of the petroleum in the barrels in which it is imported. He found that the Canadian variety did not yield evidence of these lower constituents.* SCHORLEMMER treated with nitric acid and found "nitrobenzol (from which aniline was prepared), nitrotoluol, and binitrotoluol, and small quantities of fatty acids produced from traces of olefines, which are probably contained in the crude oils."

Olefines he decided to be in very small quantity, probably because the oils he examined were the very light products known as turpentine substitute, in reality the first distillates in rectifying the crude oil. The specific gravity of this lies between ·7 and ·75. The nitric acid treatment was in consequence of no definite boiling points being attained in this liquid. The hydrides obtained were:—

	Boiling Points.	Formula.
Amyl hydride,	34° C.	C_5H_{12}
Hexyl "	68° C.	C_6H_{14}
Heptyl "	98° C.	C_7H_{16}
Octyl "	119° C.	C_8H_{18}

It was also concluded that butyl hydride, C_4H_{10}, was present in small quantities.

This experimenter found that the boiling points of the hydrocarbons of petroleum are altered very considerably by even traces of foreign substances being present, and, doubtless, the want of agreement between the boiling point assigned to any one constituent by different experimenters, is in the main due to the cause indicated.

From these facts, taken in conjunction with the phenomenon of gas springs, the main constituent of which is marsh gas, we should infer that the whole group, at least as far as $C_{15}H_{32}$, is produced in the course of the decomposition resulting in petroleum.

Still more recently an American chemist, C. M. WARREN, has very carefully and thoroughly investigated the subject, and has in many respects been led to conclusions different from those that former observers arrived at. He states that the above series of hydrocarbons, which he terms the naphtha group, does not extend farther than nonylic hydride, C_9H_{20}, and that all higher members belong to the ethylene series, in which the ratio of hydrogen to carbon atoms is always two of the former to one of the latter. Of this group he enumerates four members only, viz., those from $C_{10}H_{20}$ to $C_{13}H_{26}$ inclusive. The accuracy of his analyses, and the close approximation of the vapour density he obtained, with those theoretically assigned for the formula mentioned, together with the improved apparatus employed by him in the research, give to these conclusions very considerable weight. With respect to the liquids in the first series, moreover, he asserts that two isomeric groups exist naturally in the oil. The naphtha group, identical with the first six products obtained by PELOUZE and CAHOURS; and the

* Trans. Roy. Soc. Edin. xiii. 118, 124.
† Ann. Chem. Pharm. vi. 309. ‡ Report, liv. 15; lxi. 398.
§ J. pr. Chem. viii. 305. ‖ J. Pharm. xxvi. 549.
¶ Pogg. Ann. xxxiv. 417.
** Pharm. J. and Trans. vii. 485, and Chem. Soc. Quart. Jour. i. 248.
†† Proc. Roy. Soc. viii. 221. ‡‡ Ann. Ch. Pharm. cxiii. 151.
§§ Ann. Ch. Pharm. cxiv. 279. ‖‖ Ann. Ch. Pharm. cxv. 19.
¶¶ Comptes Rendus, vol. liv. 124; lvi. 505; lvii. 62.

* Jour. Chem. Soc. xviii. p. 54.

Beta naphtha group, composed of five members similar in composition to the first five of the naphtha group, but differing from them in that their boiling points (which this chemist determined with great exactitude) were relatively 8° higher than those of the corresponding members of the latter group.

He finds that these two groups occur as constituents of all the lighter kinds of petroleum, and that the proportion of oils belonging to the ethylene series increases with the increase in density and viscidity.

The most reliable results of the proximate analyses of petroleum are subjoined in the following table:—

NAPHTHA GROUP.

Name.	Formula.	Boiling Point.		Specific Gravity.		Vapour Density.		Composition.	
		Pelouze & Cahours.	Warren.	Pelouze & Cahours.	Warren.	Pelouze & Cahours.	Warren.	Carbon.	Hydrogen.
Ethylic hydride—ethane,....	C_2H_6	Gaseous	Gaseous	Gaseous	Gaseous	—	—	80·00	20·00
Propylic hydride—propane,..	C_3H_8	"	"	"	"	—	—	81·81	18·19
Butylic hydride — quartane or tetrane,.....	C_4H_{10}	5° to 10° / 0° to 4° *	—	·600 at 0° *	—	2·110 *	—	82·80	17·20
Amylic or pentylic hydride, or pentane,..	C_5H_{12}	30°	30°·2	·628 at 0°	·640 at 0°	2·538	—	83·33	16·67
Hexylic or caproylic hydride, or hexane..	C_6H_{14}	68°	61°·3	·669	·676	3·050	3·053	83·72	16·28
Heptylic or œnanthylic hydride, or heptane,.....	C_7H_{16}	92° to 94°	90°·4	·699	·718	3·616	3·547	84·00	16·00
Octylic or caprylic hydride, or octane,.....	C_8H_{18}	116° to 118°	119°·5	·726	·737	4·009	3·992	84·21	15·79
Nonylic or pelargonic hydride, or nonane,.....	C_9H_{20}	136° to 138°	150°·8	·741	·756	4·541	4·460	84·38	15·62
Rutylic hydride, or decane,..	$C_{10}H_{22}$	160° to 162°	—	·757	—	5·040	—	84·51	15·49
Endecane,.....	$C_{11}H_{24}$	180° to 184°	—	·766	—	5·458	—	84·61	15·39
Hydride of lauryle, or dodecane,.....	$C_{12}H_{26}$	196° to 200°	—	·776 at 20°	—	5·972	—	84·70	15·30
Hydride of cocinyle, or tridecane,.....	$C_{13}H_{28}$	216° to 218°	—	·792 at 20°	—	6·569	—	84·78	15·22
Hydride ot myristyle, or tetradecane,.....	$C_{14}H_{30}$	236° to 240°	—	—	—	7·019	—	84·85	15·15
Pentadecane,.....	$C_{15}H_{32}$	255° to 260°	—	—	—	7·523	30·16	84·90	15·10
Cetyl hydride,.....	$C_{16}H_{34}$	—		·825		·837		—	—
Candle paraffin,.....	$C_{25}H_{52}$	Solid, melting point 130° F.		·870		12·19		85·23	14·77
Ceryl hydride,.....	$C_{27}H_{56}$	" " 136° F.		—		—		85·26	14·74
Myricyl hydride,.....	$C_{30}H_{62}$	" " 143° F. / " boiling point 698° F.		·890		14·61		85·31	14·69

* Ronalds.

The last three hydrocarbons in the above series are constituents of the white crystalline paraffin which is obtained from the residuum after the lighter illuminating oils have been distilled off. Probably the missing members from $C_{17}H_{36}$ to $C_{24}H_{50}$ are also present, as well as those with 26 and 28 carbon atoms in the molecule; but sufficient evidence of their actual existence is still wanting. The first member, marsh gas, is too volatile a body to remain in the petroleum; no attempts to liquefy it thus far have been attended with success. It is doubtless the agent by whose pressure the oil is forced up to the surface when a fissure is struck by the drill.

WARREN'S BETA NAPHTHA GROUP.

	Boiling Point.	Specific Gravity.	Vapour Density.
C_4H_{10}	8° to 9°	·611 at 0°	—
C_5H_{12}	37°·0	·645	2·514
C_6H_{14}	68°·5	·689	3·038
C_7H_{16}	98°·1	·730	3·551
C_8H_{18}	127°·6	·752	3·990

Average rise of temperature of boiling point for the addition of CH_2 = 29°·9.

The main physical difference, therefore, between these two groups is, as has been said, that the members of the latter are relatively about 8° higher in boiling point than their isomers in the former, the average increment of temperature for each addition of CH_2 to the formula remaining about the same (30°·16 and 29°·9) (Warren).

TABLE OF THE THIRD SERIES (ETHYLENE OR PITTOLIUM SERIES) OF HYDROCARBONS PRESENT IN PENNSYLVANIAN PETROLEUM.

			C.	H.
Decatylene or rutylene,.....	$C_{10}H_{20}$	174°·9	85·71	14·28
Endecatylene or margarylene,..	$C_{11}H_{22}$	195°·8		
Dodecatylene or laurylene,.....	$C_{12}H_{24}$	216°·2		
Decabritylene or cocinylene,...	$C_{13}H_{26}$	235°		

Average rise of temperature of boiling point for the addition of CH_2 = 20°·6.

Some observers have stated that, besides these series, benzol and its homologues are present in crude petroleum. Warren de la Rue and Hugo Müller obtained evidence of their presence; and later, Schorlemmer has demonstrated the existence of these hydrocarbons in Canadian petroleum. † The portion of oil which came over under 150° C., when the thick black Canadian rock oil was distilled, was treated with concentrated nitric acid, which acted on it violently. The acid liquid was diluted, and the water separated from the heavy

† Proc. Royal Soc. vol. xiv. p. 168.

nitro-products, which possessed the odour of bitter almonds. "These nitro-compounds were treated with tin and hydrochloric acid, and the solution thus obtained was distilled with caustic potash. The aqueous distillate, in which some drops of an oily liquid were suspended, had the odour of aniline, and gave, with a solution of bleaching powder, the most distinct aniline reaction. The beautiful rosaniline reaction could also easily be obtained by heating one of the oily drops with bichloride of mercury. Canadian petroleum contains, therefore, the series of benzol hydrocarbons."

The question whether this series exists in Canadian petroleum in sufficient quantity to make it worth while to attempt the manufacture of aniline from the oil, is one felt to be of much importance. Upon results like the foregoing the Canadian Rock Oil Company set forth this as a probability in their prospectus; but from the fact that so many observers have never found any of these hydrocarbons, it must be considered that the amount present, if any, is so slight as not to afford any prospect of a scheme for the aniline dye manufacture proving remunerative. According to the "Annual American Encyclopædia" for 1864, the statement was current that the Humboldt Petroleum Co. of New York had works for this manufacture then (1864) in process of erection at Plummer, on Cherry Run, Venango County, Pennsylvania; and that the company had already produced several superior aniline dyes. We are not, however, aware that any corroboration of this statement exists. For details of the properties and reactions of this doubtful series of constituents we will commend our readers to any manual of organic chemistry.

As has been remarked, the name paraffin has been given to the group of hydrocarbons forming the main portion of natural petroleum, in consequence of the fact that the members are not easily affected by chemical reagents.

In the cold they are not acted on by any of the more powerful, commonly recurring acids, even a mixture of fuming nitric and sulphuric acids being powerless to effect oxidation. By the aid of heat, however, they may be oxidised, even by dilute nitric acid, carbonic acid gas and water being the principal products, accompanied by small quantities of fatty acids, succinic acid, and nitriles.

When chromic acid is heated with them, more or less acetic acid is found amongst the products (Schorlemmer). When chlorine and bromine act upon these bodies, substitution products are formed; two atoms of chlorine usually sufficing to withdraw one hydrogen atom, which unites to form hydrochloric acid with the one, and is itself replaced by the other.

Thus from marsh gas, CH_4, the four substitution products, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, have been obtained. Similarly the six hydrogen atoms of the second member (ethane, C_2H_6) have been severally replaced by chlorine. Propane and hexane have thus far only yielded compounds in which part of the hydrogen is thus replaced, the highest containing six chlorine atoms.

It is difficult to obtain a pure monochloride by passing chlorine into the liquid paraffin, in consequence of the portions of monochloride first formed being attacked and converted into compounds containing two, three, or four chlorine atoms before all the hydrocarbon has been acted on. This complication may, however, be prevented by bringing chlorine in contact with the vapour of the boiling hydrocarbon; the less volatile monochloride, condensing as soon as it is formed, escapes the further action of the gas (Schorlemmer).

Iodine has no action at all on these bodies, and that of bromine is similar in kind but much less energetic than that of chlorine.

A substitution, inverse to that described above, takes place when such chlorides, bromides, or iodides (which can be obtained by other means), are treated with zinc and hydrochloric acid, the nascent hydrogen replacing the chlorine, &c., with which a further portion unites to form hydrochloric, hydrobromic, or hydriodic acid.

By the action of potash or soda upon these chloro-, bromo-, or iodo- derivatives of the paraffins (haloid derivatives, as they are called), the haloid element may be replaced by the grouping (OH), and a series of bodies (CH_3OH, C_2H_5OH, C_3H_7OH, &c.) formed, known as the class of monatomic alcohols. The best known members are methylic alcohol, CH_3OH (hydrate of methyl), which occurs in wood spirit, ethylic alcohol, C_2H_5OH (hydrate of ethyl), which forms the basis of all ordinary alcoholic liquors, and the fifth member, amylic alcohol, $C_5H_{11}OH$ (hydrate of amyl), which forms the principal constituent of fusel oil.

These bodies differ from the corresponding paraffins (which are often regarded as the hydrides of the radicals mentioned here) in that each contains an atom of oxygen united to the elements forming the hydrocarbon.

The other constituents of petroleum may be separated from the paraffins by treating the mixture of oils with sulphuric acid, and afterwards with fuming nitric acid, or a mixture of nitric and sulphuric acids, the other substances being either oxidised or converted into nitro-compounds, which are either dissolved by the acids or are much less volatile than the hydrocarbons. After washing with water, drying over caustic potash, and rectifying over sodium, the distillate will consist only of paraffins (Schorlemmer).

The members of series of radicals known as olefines (C_2H_4, &c.) are acted on readily by chlorine, bromine, and iodine, the first uniting with them to form dichlorides—compounds isomeric with the dichloro-substitution products of corresponding paraffins—the other two forming similar combinations. Hydrochloric, hydrobromic, and hydriodic acids also unite with them, forming compounds identical in composition with the mono-substitution products of the paraffins. With other acids, too, these bodies unite no less readily; with sulphuric acid compounds analogous with sulphovinic acid, $C_2H_5HSO_4$, may be formed; the action of hypochlorous acid upon ethy-

lene (or ethene) results in the formation of ethylene chlorhydrate, C_2H_4ClOH. Hypobromous acid acts similarly.

A series of alcohol may be obtained from the haloid derivatives of the olefines by reactions analogous to those employed in the former case. Thus, ethene iodide, $C_2H_4I_2$, treated with silver acetate, yields ethene diacetate and silver iodide; the former may be decomposed by an alkali with formation of ethene dihydrate, or ethene alcohol and acetate of the alkali metal. The members of this series of alcohols possess a very sweet taste, and are accordingly known as glycols.

Illuminating Power.—This has been examined by Dr. C. F. Chandler, in conjunction with Dr. J. G. Pohle and E. G. Kelly, and from the results they obtained we abstract the following:—

A sperm candle burning 2 grains per minute was taken as the standard of comparison. The oils tested were entered for competition at the American Institute Fair, the gentlemen we have named being appointed judges of their relative values. These oils may be taken as the safest varieties of American oils, as may be seen from the statement of their flashing and burning points.

	Specific Gravity.	Flashing Point. Inflammable Vapour Evolved.	Burning Point. Oil takes fire.
Registered by the Board of Health Ordinance,		100° Fahr.	110° Fahr.
Standard kerosene.....	46° B.	115° "	128° "
Astral oil,.....	49° B.	125° "	138° "
Mineral sperm,.....	36° B.	262° "	300° "

The standard kerosene and astral oil are superior varieties of kerosene. The mineral sperm has been described under petroleum products. Its high gravity prevents its being readily taken up by the usual flat wick, and renders it much more serviceable when burned in an Argand lamp with circular wick, in which the level of the oil more nearly approaches the top of the wick. The dual burner, also, which contains two flat wicks side by side, burns this oil very readily and completely.

The following table shows the rate of consumption and illuminating power of these oils:—

Name of the Oil.	Hours required to Burn 1 Gallon of Oil.	Average Candle Power of the Flame.	Pounds of Candles equivalent to 1 Gallon of Oil.	Hours required to Burn a Gallon, at rate of Eight Candles Power.
I. Low glass lamp, $\frac{3}{8}$ inch flat wick—				
Standard kerosene,.....	200	4·26	14·60	106·5
Astral oil,.....	179·5	4·77	14·67	107·
II. High glass lamp, $\frac{5}{8}$ inch flat wick—				
Standard kerosene,.....	109	8·9	16·63	121
Astral oil,.....	112	7·7	14·78	108
III. German student lamp, argand circular wick—				
Standard kerosene,.....	69	14·7	17·38	127
Astral oil,.....	81·6	11·1	15·52	113
Mineral sperm,.....	90	11·6	17·89	130·5
IV. Merrill's patent lamp, argand circular wick—				
Standard kerosene,.....	94·5	12·	19·44	142
Astral oil,.....	102·5	11·47	20·15	147
Mineral sperm,.....	105·5	11·83	21·39	156
V. High glass lamp, "dual burner" A, 2 flat wicks $\frac{5}{8}$ inch wide—				
Standard kerosene,.....	93	9·60	15·30	112
Mineral sperm,.....	130	8·16	18·18	133
VI. High glass lamp, "dual burner" B, 2 flat wicks $\frac{7}{8}$ inch wide—				
Standard kerosene,.....	59	17·50	17·70	129
Mineral sperm,.....	78	14·30	19·12	139·5

Summarizing these results, it would appear that in flat-wicked lamps of the usual size the illuminating power of the kerosene flame equals that of eight to nine sperm candles; with the round wick, that of eleven to fifteen; with the dual burner, from nine to seventeen; and that a gallon of oil lasts from 59 to 109 hours in such lamps, and gives an amount of light equivalent to that which is afforded by from $14\frac{1}{2}$ to 20 lbs. of sperm candles.

A gallon of mineral sperm is thus seen to give an amount of light equal to that of from 18 to $21\frac{1}{2}$ lbs. sperm candles, and to this it adds the advantage of equalling whale oil in degree of safety.

Premising that an ordinary burner, burning 5 feet of gas per hour, gives, if the gas be of good quality, a light equal to sixteen candles, we may argue that the light given by these varieties of refined oil, as compared with that of coal gas, is given in the following table:—

Kind of Lamp.	One Gallon Standard Kerosene Equals.	One Gallon Astral Oil Equals.	One Gallon Mineral Sperm Equals.
	Feet Gas.	Feet Gas.	Feet Gas.
In flat-wick lamp,.....	302	270	—
In German student lamp,	317	282	326
In Merrill's lamp,.....	355	367	390
In dual wick " $\frac{5}{8}$ inch,.	280	—	332
" " $\frac{7}{8}$ "	322	—	349
Average,.....	315	306	349

Dr. Frankland has experimented upon the illuminating power of petroleum and other lighting materials, and concludes that the quantities of dif-

ferent substances required to produce the same amount of light are relatively as follows:—

Young's paraffin oil,	1 gallon
American rock oil, No. 1,	1·26 "
" " 2,	1·30 "
Paraffin candles,	18·6 lbs.
Sperm "	22·9 "
Wax "	26·4 "
Stearic "	27·6 "
Composite "	29·5 "
Tallow "	36· "

From these results the comparative cost from different sources of the light of twenty spermaceti candles, each burning for ten hours, at the rate of 120 grains per hour, may be calculated—

	s.	*d.*
Wax,	7	2½
Spermaceti,	6	8
Tallow,	2	8
Sperm oil,	1	10
Coal gas,	0	4¼
Cannel gas,	0	3
Paraffin,	3	10
Paraffin oil,	0	5
Rock oil,	0	6½

Thus, in an economical point of view, the rock oil and the paraffin oil approach gas much more closely than any other illuminating agent hitherto invented; while the enormous quantities in which they are now being produced cannot fail to make them still lower in price. Therefore we may look upon them as very formidable rivals of gas light.

In the third table we have the amount of carbonic acid and heat generated per hour by various illuminating agents, each giving the light of twenty sperm candles—

	Carbonic Acid.		Heat.
Tallow,	10·1	cubic feet	100
Spermaceti, Wax,	8·3	"	82
Paraffin,	6·7	"	66
Coal gas,	5·0	"	47
Cannel gas,	4·0	"	32
Paraffin oil, Rock oil,	3·0	"	29

This table shows to what extent the atmosphere of rooms is deteriorated by these illuminating agents. It shows also that, from this point of view, paraffin and rock oils stand out as the best sources of light.

Experiments have been from time to time instituted with a view to the profitable production of illuminating gas from petroleum. George Bower* has given much time to this problem, and concludes that petroleum gas, though not so cheap as coal gas, is very much less costly than either tallow or the oil as ordinarily burnt in lamps.

In order to obtain the maximum of illuminating power from petroleum gas, Bower uses what is known as the double form of retort, without anything in it (the use of coke, broken bricks, &c., to give surface having been tried and abandoned). The retort is heated to a moderate heat, dull cherry-red by daylight; and though the yield of gas is small, it gives more than double the light obtained from gas produced at a higher temperature. His estimate of the cost of petroleum gas is as follows:—

* Journ. Soc. Arts, July, 1863, p. 617.

	s.	*d.*
15 gallons of oil at 1*s.*	15	0
Coke to heat the retorts, 3 cwts., at 1*s.*	3	0
Labour, part of a lad or man's time,	1	6
Wear and tear,	0	9
Interest on capital,	0	4
Fund to maintain plant in perpetuity,	0	6
Net cost of 1200 cubic feet,	£1	1	1

"This is about five times what coal gas would cost made on the same scale; but as the illuminating qualities of the 1200 cubic feet are equal to about 3500 of ordinary coal gas, the oil does not compare very unfavourably."

This manufacture of petroleum gas is in actual operation in New York and other United States cities; the naphtha which cannot be safely used in oil lamps being thus turned to profitable account. The gas so produced is not used alone, however, but is mixed with coal gas in the gasholders connected with the mains.

In the works of the New York Mutual Gas Company "the liquid naphtha flows from the reservoir to the retort house, where it is received in four stills, within which are steam pipes. The vaporized naphtha passes next to a row of clay retorts, forty-eight in number, similar to those used for making coal gas, except that they are double. In the same building there are 240 retorts for making the coal gas that is to be mixed with the naphtha gas. The passage of the vaporized naphtha, through and over the red hot retorts, converts it into as rich an illuminating gas as that from the best cannel coal. Thence the gas passes into the condensers, thence to a station meter, and thence to the gasholders, where it mixes with the ordinary coal gas.

Use as Fuel.—Besides its primary use as an artificial illuminant, petroleum has been found to subserve to many useful purposes, notably as a fuel. In some of the periodicals specified below a great deal has been written on the question of the practicability of employing it for heating the steam boilers, both of ordinary locomotive engines and of sea-going steamers, and from these sources we extract the more important conclusions at which some of the writers have arrived.

MM. H. Sainte Claire Deville and C. Dieudonné have tested the practicability of employing petroleum and coal oil in locomotives, and report very favourably thereon. A lengthy description of the modifications necessary to be adopted in using this species of fuel in the usual locomotive engine will be found in the "Comptes Rendus," vol. lxviii. p. 350 (Feb. 15, 1869), and vol. lxix. p. 933 (Nov. 2, 1869), and in the "Annales de Chimie et de Physique," Sept. 1868. The application of the principle involved is due to M. Paul Audouin, the writer of the last mentioned article, and in the present instance the alterations were made by M. Dieudonné under M. Deville's direction. The cost of making such alterations did not exceed 900 francs (£37); one of the two engines, placed at the disposal of the two latter gentlemen, was tried between Epernay and Paris, and was found to travel at a speed of 46

kilomètres (28½ miles) an hour, on a line of which the greatest ascent was 8·8 feet per mile. The consumption of oil was remarkably uniform, 12 lbs. per mile. During its service (which continued for some time) at the depot at Flamboin, the amount of consumption of oil, as compared with the distance travelled, was 21 lbs. per mile; whilst, during the same period, the amount of coke used by engines of the same kind was 32½ lbs. per mile.

With regard to its use as a fuel for steamers, much has been said on both sides. Three commissioners, including the chief engineer of the United States navy, were appointed by the American government to look into this subject. They were instructed to report on "the relative evaporative powers of the oil as compared with anthracite coal, the practicability of its use, if unattended with danger, and to set forth its advantages, if any." In reply to the first inquiry, they stated that it is 103 per cent. superior to anthracite coal; that the time required for generating steam to 20 lbs. pressure was only 28 minutes, against 60 for anthracite. The commissioners recommended the secretary of the navy to introduce the oil on board one of the government steamers, to determine practically its economical efficiency. The advocates for its introduction contend that, in a vessel like the Cunard steamer *Persia*, the saving, taking into account the smaller space required and all other advantages, would amount to £2400 per trip. The process for adapting the oil for this purpose was patented by Shaw and Linton of Philadelphia. These calculations as to economy seem to have been based on the idea that even with the increased demand the price of petroleum would remain as it was, and also upon the cost of coal in America, not in England. "Should the results," it is added, "equal what may be fairly anticipated, steam navigation will be revolutionized; a war steamer with oil fuel could hold the sea twice as long as now, and lines of commercial communication now too far apart from the difficulty of carrying a sufficient quantity of coal, would be then formed with ease. Direct lines from New York to Australia, and between California and China, would then be of easy accomplishment."

This report was criticized on this side the Atlantic with considerable warmth, and not a few persons believed that in a short time coal would be superseded altogether as a fuel for the vessels of our navy. In a few months experiments were set on foot at Woolwich Dockyard to test the value of these hydrocarbons for steam fuel; and whilst these experiments were going on Dr. B. H. Paul, and some others who had specially studied the subject, put the matter in its true light, and showed conclusively that the scheme was utterly impracticable. Dr. Paul says,* "In the first place, one of the chief alleged advantages of petroleum over coal was that it would lie in small compass and make a less demand on space and tonnage than coal does; since with petroleum in the place of coal two-thirds of the space required for fuel in a steam vessel would be saved and steam ships might keep at sea three times as long as at present. Then, coal depôts would be unnecessary for steam packets on the longest lines of ocean navigation; and since no stokers would be needed in using petroleum, a whole army of employés might be dispensed with.

"Now the specific gravity of coal is from 1·24 or 1·44 to 1·6, while that of petroleum is from ·800 to ·850, consequently the weight of a cubic foot of these materials would be respectively about as follows:—

	Lbs.	Lbs.	Lbs.
Coal,	77·4	90	100
Petroleum,	—	50	53

But since petroleum, being liquid, lies in a more compact manner than coal, in estimating the spaces occupied by these materials, allowance should be made for the interstices or empty spaces between the lumps of coal. Taking this as amounting to one-third of the whole bulk of a heap of coal—which is a liberal allowance—the contents of a cubic foot would be as follows:—

	Lbs.	Lbs.	Lbs.
Coal,	52	60	70
Petroleum,	—	50	53

So that the spaces occupied by equal weights of coal and petroleum would be as 1 is to 1·2 or 1·4.

"Then the relative heating power of equal weights of coal and petroleum would depend upon their respective chemical composition, which may be compared as follows for 100 parts:—

	Coal.	Petroleum.
Carbon,	83	85
Hydrogen,	5	15
Ash, &c.,	—	—
	100	100

Accordingly the relative heating power of equal weights of coal and petroleum would be in the following ratio:—

	Coal.	Petroleum.
Calorific power,	1·02	1·50

And the spaces occupied by quantities of petroleum and coal, having equal heating power, would be in the ratio of 1 to 1·16.

"The difference in favour of petroleum is in itself too small to admit of any advantage being gained in regard to stowage, and it is more than doubtful whether there be any other advantageous difference between petroleum and coal for fuel.

"It must also be considered how far the difference between the prices of petroleum and coal would have the effect of neutralizing the above, or any other advantage to be gained by the use of petroleum as fuel. The price of petroleum varies from £15 to £20 a ton, while that of coal for steam vessels is under £1 per ton at any part of the British coast, and even at the coaling stations in the East it does not exceed £2 10*s.* to £3 10*s.* per ton.

"In addition to this, the highly inflammable nature of petroleum must be considered. Its storage on board a ship would require the use of air-tight vessels, and even then there might be

* Chem. News, vol x. p. 292. See also vol. xi. p. 63.

considerable risk of the production of explosive mixtures of petroleum vapour and air. But what would be the condition of a ship of war provided with petroleum as fuel if a shot penetrated the vessel containing the petroleum, and allowed it to escape into the proximity of the boiler fires?"

A writer in the *American Artizan** adds to these pretty conclusive reasons the enormous cost of applying the apparatus known as FOOTE'S retort apparatus for burning the oil to steam vessels, the cost probably amounting to from 40,000 dols. to 60,000 dols. per ship. The high temperature, too, to which this apparatus is necessarily exposed would make it requisite that portions should be constantly renewed; and the deposition of carbon, coke, and incombustible matter within the retorts and pipes is so great, that in one case the pipes became so choked in less than forty-eight hours that the fire went out, and could only be renewed by taking the fixture apart and cleaning it.

Moreover, the evaporative power obtained in actual practice is not so different from that of coal as theory would indicate. The experiments carried on with the machinery of the United States gunboat *Palos* in Boston harbour show this. The result of these trials was, that if the evaporative power of anthracite be represented by 1, that of petroleum is 1·38, and not 1·835, as we might suppose from theoretical considerations.

In accordance with these opinions, and after careful and long-continued trials, the secretary of the United States' navy finally reported against the use of petroleum as a fuel in steamships. He says:—"The Act approved April 17, 1866, appropriated 5000 dollars for testing the use of petroleum as a fuel for marine boilers. An elaborate series of experiments has been made at the New York and Boston navy yards. The conclusion arrived at is, that convenience, comfort, health, and safety are against the use of petroleum in steam vessels, and that the only advantage thus far shown is not a very important reduction in bulk and weight of fuel carried." For further information on this subject we refer our readers to articles by Dr. PAUL in the *Journal of the Society of Arts*, vol. xvi. pp. 401 and 837; by Professer RANKINE, *Journ. of the United Service Institution*, xi. 218; and by Captain SELWYN, R.N., and C. J. RICHARDSON, *Journ. Soc. Arts*, vol. xvi. pp. 407 and 504.

The use of naphtha or benzine under the name of turpentine substitute has been already mentioned. The varying nature of the liquid has caused corresponding difference of opinion respecting its utility; but we believe that when a good sample is procured, it may be most efficiently employed by painters.

In America much of this light oil is sold after having been subjected to some ridiculous and totally inefficient process (protected by a patent), which professes to rob the oil of its dangerous constituents. "Liquid gas," "aurora oil," "safety gas," "pusoline," &c., are some names of such dangerous oils. By their use many terrible accidents have arisen.

Curriers use an oil prepared from petroleum for finishing leather, which is said to be preferable to the fish and neatsfoot oil hitherto employed. A soap for toilet use has also been made, which contained petroleum incorporated with the fat and alkali. Its manufacture has not yet proved a perfect success, owing to the odour derived from the original petroleum. The hopes of those who trusted to employ the oil as a source of aniline colours has not, as far as we can ascertain, yet been realized.

In medicine and pharmacy gasoline has been employed as a disinfectant. Dr. DAY, of Geelong, states that it either contains a large quantity of peroxide of hydrogen or possesses the property of generating this valuable oxidising agent. When unglazed paper or any porous substance is brushed over with gasoline, it will at once give the reaction for hydrogen peroxide, and will continue to do so for a year or more. Dr. DAY recommends that books, newspapers, &c., that have been used by fever patients, or kept in their apartments, be disinfected by brushing them over with gasoline.

Preparations have recently been introduced, as bases for the various ointments, under the names of "cosmoline" and "vaseline," which are the softer paraffins of native petroleum purified by treatment with animal charcoal. The fact that they do not become rancid, like so many natural fats hitherto employed, renders them very applicable to this purpose.

In view of the danger to be apprehended from the careless storage, &c., of petroleum, an Act is in force to prevent, as far as possible, accidents from this cause. It is intituled "An Act for the Safe Keeping of Petroleum and other Substances of a like Nature, 21st August, 1871." From it we extract some of the more important sections:—

3. For the purposes of this Act, the term "Petroleum" includes any rock oil, Rangoon oil, Birmah oil, oil made from petroleum, coal, schist, shale, peat, or other bituminous substances, and any products of petroleum, or any of the above-mentioned oils; and the term "petroleum to which this Act applies," means such of the petroleum so defined as, when tested in manner set forth in Schedule One to this Act, gives off an inflammable vapour at a temperature of less than 100° Fahr.

5. The owner or master of any ship carrying a cargo, any part of which consists of petroleum to which this Act applies, on entering any harbour within the United Kingdom, shall give notice of the nature of such cargo to the harbour authority having jurisdiction over such harbour. If such notice is not given, the owner and master of such ship shall each incur a penalty not exceeding the sum of £500, unless it is shown to the satisfaction of the court before which the case is tried that neither the owner nor the master knew the nature of the goods to which the proceedings relate, nor could with reasonable diligence have obtained such knowledge.

6. Where any petroleum to which this Act applies

* Chem. News, vol. xvii. 224.

(*a.*) is kept at any place, except during the seven days next after it has been imported; or (*b.*) is sent or conveyed by land or water between any two places in the United Kingdom; or (*c.*) is sold or exposed for sale; the vessel containing such petroleum shall have attached thereto a label in conspicuous characters, stating the description of the petroleum, with the addition of the words "highly inflammable;" and with the addition, (*a.*) in the case of a vessel kept, of the name and address of the consignee or owner; (*b.*) in the case of a vessel sent or conveyed, of the name and address of the sender; (*c.*) in the case of a vessel sold or exposed for sale, of the name and address of the vendor. All petroleum to which this Act applies which is kept, sent, conveyed, sold, or exposed for sale, in contravention of this section, shall, together with the vessel containing the same, be forfeited; and in addition thereto, the person keeping, sending, selling, or exposing for sale, the same shall for each offence be liable to a penalty not exceeding £5.

7. Save as hereinafter mentioned, after the passing of this Act, petroleum to which this Act applies shall not be kept, except in pursuance of a license given by such local authority as is in this Act mentioned. All petroleum kept in contravention of this section shall, together with the vessel containing the same, be forfeited; and in addition thereto, the occupier of the place in which such petroleum is so kept shall be liable to a penalty not exceeding £20 a day for each day during which such petroleum is so kept. This section shall not apply to any petroleum kept either for private use or for sale, provided the following conditions are complied with:—(1.) That it is kept in separate glass, earthenware, or metal vessels, each of which contains not more than a pint, and is securely stopped: (2.) That the aggregate amount kept, supposing the whole contents of the vessels to be in bulk, does not exceed 3 gallons.

8. The following bodies shall respectively be the local authority to grant licenses under this Act in the districts hereinafter mentioned; (that is to say) (1.) In the city of London, except as hereafter in in this section mentioned, the court of the lord mayor and aldermen of the said city: (2.) In the metropolis (that is, in places for the time being within the jurisdiction of the Metropolitan Board of Works under the Metropolis Management Act, 1855), except the city of London, and except as hereafter in this section mentioned, the Metropolitan Board of Works: (3.) In any borough in England or Ireland, except as hereafter in this section mentioned, the mayor, aldermen, and burgesses, acting by the council: (4.) In any place in England or Ireland, except as hereafter in this section mentioned, within the jurisdiction of any trustees or improvement commissioners appointed under the provisions of any local or general Act of Parliament, and not being a borough or comprising any part of a borough, the trustees or commissioners: (5.) In any place in England, except as hereafter in this section mentioned, within the jurisdiction of a local board, constituted under the Local Government Act, 1858, and not being any of the districts before mentioned or comprising any part of any such district, the local board: (6.) In any borough in Scotland, except as hereafter in this section mentioned, the town council: (7.) In any place in Scotland, except as hereafter in this section mentioned, within the jurisdiction of police commissioners or trustees exercising the functions of police commissioners under any general or local Act, and not being a borough or comprising any part of a borough, the police commissioners or trustees: (8.) In any harbour within the jurisdiction of a harbour authority, whether situate or not within the jurisdiction of any local authority before in this section mentioned, the harbour authority, to the exclusion of any other local authority: (9.) In any place in which there is no local authority as before in this section defined, in England or Ireland, the justices in Petty Sessions assembled, and in Scotland any two or more justices of the peace for the county sitting as judges in the Justice of Peace Court.

9. Licenses in pursuance of this Act shall be valid if signed by two or more of the persons constituting the local authority, or executed in any other way in which other licenses, if any, granted by such authority are executed. Licenses may be granted for a limited time, and may be subject to renewal or not in such manner as the local authority think necessary.

11. Any officer authorized by the local authority may purchase any petroleum from any dealer in it, or may, on producing a copy of his appointment, purporting to be certified by the clerk, or some member of the local authority, or producing some other sufficient authority, require the dealer to show him every or any place, and all or any of the vessels in which any petroleum in his possession is kept, and to give him samples of such petroleum on payment of the value of such samples.

The directions for testing petroleum in order to ascertain if it come within the Act or not are given in Schedule One of the Act, as follows:—

Directions for Testing Petroleum to ascertain the Temperature at which it gives off Inflammable Vapour.—The vessel which is to hold the oil shall be of thin sheet iron; it shall be 2 inches deep and 2 inches wide at the opening, tapering slightly towards the bottom; it shall have a flat rim with a raised edge one quarter of an inch high round the top; it shall be supported by this rim in a tin vessel 4½ inches deep and 4½ inches in diameter; it shall also have a thin wire stretched across the opening, which wire shall be so fixed to the edge of the vessel that it shall be a quarter of an inch above the surface of the flat rim. The thermometer to be used shall have a round bulb about half an inch in diameter, and is graduated upon the scale of Fahr., every 10° occupying not less than half an inch upon the scale.

The inner vessel shall be filled with the petroleum to be tested, but care must be taken that the liquor does not cover the flat rim. The outer vessel shall be filled with cold, or nearly cold, water; a small flame shall be applied to the bottom of the outer vessel, and the thermometer shall be inserted into

the oil so that the bulb shall be immersed about $1\frac{1}{2}$ inch beneath the surface. A screen of pasteboard or wood shall be placed round the apparatus, and shall be of such dimensions as to surround it about two-thirds, and to reach several inches above the level of the vessels.

When heat has been applied to the water until the thermometer has risen to about 90° Fahr., a very small flame shall be quickly passed across the surface of the oil on a level with the wire. If no pale-blue flicker or flash is produced, the application of the flame is to be repeated for every rise of 2° or 3° in the thermometer. When the flashing-point has been noted, the test shall be repeated with a fresh sample of the oil, using cold, or nearly cold, water as before; withdrawing the source of heat from the outer vessel when the temperature approaches that noted in the first experiment, and applying the flame test at every rise of 2° in the thermometer. This, the English standard tester, is represented in Fig. 26.

Fig. 26.



Much dissatisfaction has been felt and expressed about the official method of testing petroleum; and in 1876 Professor Abel was requested by the government to ascertain by experiment whether the method was such as uniformly to insure reliable and satisfactory results; if not, could a method be devised which would do this, remembering that in many cases the examination would be carried on by comparatively inexperienced persons. Professor Abel considered that the method referred to was not "such as uniformly to insure reliable and satisfactory results." With this opinion Boverton Redwood, secretary to the Petroleum Association; T. W. Keates, chemist to the Metropolitan Board of Works; Dugald Campbell, and others much experienced in petroleum testing, fully coincided. After much investigation, Professor Abel contrived an apparatus, which is stated by two of the gentlemen just mentioned, as well as by others, to remedy the defects of the former system.

The new system proposed has the following peculiarities:—The water bath is provided with an external air chamber, and a similar air space surrounds the oil cup. The experiment is commenced with water in the bath at a temperature of 130°, and the oil is slowly raised to its flashing point, without the aid of a lamp, by the transmission of heat through the air surrounding the cup, while the loss of heat by radiation from the external surface of the water bath is prevented by the outer air space. The oil cup is strictly a closed vessel, provided with a central orifice covered by a slide. A small swinging test lamp, supported by trunnions on a couple of standards fixed to the lid of the cup, is kept constantly burning during the experiment, with a flame 0·15 of an inch in diameter. The little lamp is fed with colza oil, or gas may be used where convenient. As the slide which covers the central orifice is withdrawn in testing, a pin or stud, fixed to its upper surface, comes into contact with the swinging lamp, and causes it to be tilted so that the test flame is brought to the opening in the lid of the cup. At the same time that the central orifice is thus uncovered, a smaller opening on either side is disclosed, and these serve to admit fresh air to the vapour chamber. The movement of the slide is timed by a pendulum (a weight fastened to a cord 2 feet in length) placed in front of the operator, the slide being slowly drawn open during three oscillations, and closed during the fourth. The test flame is to be applied in this manner once for every rise of 1° in the thermometer. A standard apparatus is to be placed in charge of some authority (*e.g.*, the Weights and Measures Office), and every apparatus is to be tested and stamped, so as to be identified as a legal apparatus.

With a view of indicating the reliable character of the new test, a table is given of the flashing points of a number of samples, determined in duplicate and triplicate, the results showing in many cases an exact concordance, and in no case a larger variation than 1°.

This mode is in reality a "close test," *i.e.*, the petroleum vapour is not, whilst the oil is being heated, allowed to diffuse into the atmosphere, but is confined; the cover only being removed when the light is applied. One difficulty up to the present has been in the fact, that under these circumstances the oil does not "flash" at the same temperature as when the "open test" (that legally directed) is employed; and experts have never been agreed what number of degrees of temperature should be allowed for this difference. Now, however, T. W. Keates (who devised a close test in 1872, of which this is a modification), Boverton Redwood, and Professor Abel are of the opinion that in the apparatus just described, the temperature 73° Fahr. is equiva-

lent to 100° Fahr. under the "open test" of the Petroleum Act. In a short time, therefore, there is every probability that Professor ABEL'S apparatus will replace this.

Commerce in Petroleum.—The production of petroleum increased very rapidly, from the time of its assuming; a commercial importance in 1859, until 1874; since then it has fallen off a little, as the following table will show:—

PRODUCTION OF CRUDE PETROLEUM IN THE PENNSYLVANIA OIL REGIONS (BOURGOUGNON).

Year.	Barrels (42 Gallons each).	Year.	Barrels (42 Gallons each).
1859	82,000	1868	3,715,700
1860	500,000	1869	4,215,200
1861	2,113,600	1870	5,659,000
1862	3,056,700	1871	5,800,000
1863	2,611,300	1872	6,300,000
1864	2,116,100	1873	9,883,000
1865	2,497,700	1874	10,925,973
1866	3,597,700	1875	8,788,506
1867	3,347,300	1876	8,968,306

Of the present production, about 31,000 barrels daily average, by far the greater portion is refined in the United States, which consumes 6000 barrels of the refined oil; two-thirds being supplied by the Cleveland refineries, New York and Pittsburg refining one-sixth, and other small places the remainder.

The total exports of petroleum, crude and refined, and naphtha from the United States, for the years 1873, 1874, and 1875, were—

Exports.	1873. Gallons.	1874. Gallons.	1875. Gallons.
Crude,	19,643,740	14,430,851	15,141,295
Refined,	209,021,305	208,635,382	203,471,470
Naphtha,	10,250,547	10,617,268	13,799,112
Total,	238,915,592	233,683,501	232,411,877

Germany has been and continues to be the chief European customer for petroleum, taking in 1874 42,000,000 gallons from the port of New York alone, whilst the United Kingdom took 20,000,000 gallons.

The following numbers will give the amounts of the various petroleum products imported into the United Kingdom during the past six years; they are taken from the *Oil Trade Review*. The barrels contain each 42 gallons, the cases 10 gallons.

Year.		Refined.	Kerosene.	Lubricating Oil.	Residuum.	Petroleum Spirit, Benzoline, or Naphtha.	
		Barrels.	Cases.	Barrels.	Barrels.	Barrels.	Cases.
1871	London,	119,291	10,605	2,555	—	29,934	3,125
	Total,	218,049	19,900	4,275	3,172	76,792	16,625
1872	London,	59,640	8,362	504	—	33,010	400
	Total,	141,076	8,812	1,953	4,355	66,906	1,900
1873	London,	209,451	18,828	7,828	—	44,555	—
	Total,	368,715	19,700	12,038	12,180	80,900	6,250
1874	London,	259,005	15,765	9,254	150	51,219	100
	Total,	486,559	20,175	9,315	47,139	103,584	700
1875	London,	169,762	3,250	2,511	1,000	53,173	—
	Total,	326,963	7,484	3,346	39,745	101,289	—
1876	London,	232,505	7,283	5,663	1,286	61,211	200
	Total,	480,917	15,233	6,920	56,803	124,185	200

The distribution of this to the various ports was in 1876 as follows:—

	Petroleum, Oil, &c.		Lubricating Oil.	Residuum.	P. S. or Benzoline.	
	Barrels.	Cases.	Barrels.	Barrels.	Barrels.	Cases.
London,	232,505	7,283	5,663	1,286	61,211	200
Liverpool,	150,494	6,950	434	50,324	41,052	—
Hull,	25,566	—	—	—	6,851	—
Bristol,	47,701	1,000	—	—	15,071	—
Clyde and Leith,	280	—	823	5,193	—	—
Dublin,	24,371	—	—	—	—	—

Of the petroleum coming into London by far the largest part is, before being sold, tested by the chemist of the Petroleum Association, at present Mr. BOVERTON REDWOOD, to whom we are indebted for much valuable information. This association during the twelve months ending May 31, 1877, tested samples representing a total of 234,728 barrels, against 219,960 barrels for the previous year, and 136,758 for the twelve months ending May 31, 1875. The amount rejected on account of its objectionable odour or colour, or low flashing point, was in year 1876 to 1877, of the United States oils ·73 per cent., and of the Canadian product 6·37 per cent. of the whole amount examined.

PARAFFIN.—This name is chemically applied to the whole class of hydrocarbons of the general formula, C_nH_{2n+2}, of which class marsh gas, CH_4, is the first member, and the members of which are present in the various kinds of petroleum. It is, however, more generally restricted to the members of that series which have many—twenty or more—carbon atoms in the molecule, and which form at ordinary temperatures a solid white crystalline mass. The heavy oil containing this in solution is termed "paraffin oil." It is in this sense that the word paraffin is used in this article, the other members of the chemical class paraffins having been noticed under PETROLEUM.

As has been indicated (vide ante, *Petroleum Products*), paraffin is contained in and prepared from

petroleum, 1 to 2 per cent. of the crude oil being its usual proportion. By far the greater proportion, however, of that in commerce is obtained, not from the natural oil, but from the oils distilled by artificial means from bituminous shales.

In 1830 REICHENBACH obtained from the tar produced when the wood of the red beech was destructively distilled a white crystalline body, to which he gave the name of "paraffin," on account of its being difficultly acted on by chemical agents. A year later Dr. CHRISTISON of Edinburgh obtained the same substance from Rangoon petroleum, and named it "petroline." From these sources it was obtained in small quantities and with much labour, so that it remained for many years merely a chemical curiosity. In 1847, however, JAMES YOUNG of Glasgow having, at Dr. LYON PLAYFAIR'S request, examined a petroleum exudation in a coal mine near Alfreton, Derbyshire, found paraffin in it, and established works there to refine the oil and bring this new product, paraffin, into commerce.

In a few years the supply of oil was exhausted, and YOUNG conceived the happy idea of seeking in the oil, which had even before that time been distilled from coals, for this substance which he had been obtaining from the natural oil.

The distillation of bituminous shale for illuminating oils had originated more than a century and a half before this, for in 1694 a patent was granted to HANCOCK, PORTLOCK, and MARTIN EELE, for the manufacture of "pitch, tar, and oils," from a kind of stone. In 1716 Messrs. BETTON of Shrewsbury, and in 1781 the EARL OF DUNDONALD, distilled oil from bituminous shales. Similar patents were granted in France in 1824 to M. CHERVEAU, and in 1832 to MM. BLUM and MONEUSE. LAURENT, the eminent chemist, and afterwards SELLIGUE, conducted the operations of these latter gentlemen at a factory of M. MONEUSE near Autun, Saône-et-Loire, and by them the distillation and subsequent purification of coal oil products was carried to what is even now recognized as a high degree of perfection. SELLIGUE, between the years 1838 and 1843, manufactured about 15,000 barrels of shale oil.

In a very short time, however, after YOUNG turned his attention to this industry, it grew from being one of little importance to occupy a most important position in the commercial world, so that YOUNG may justly be considered the "father of the coal oil industry." Within the short space of twenty years it attained such magnitude that, in 1873, it gave employment to 7000 men, who earned about £10,000 weekly in wages. At that time 800,000 tons of shale were distilled yearly, producing 30,000,000 gallons of shale oil, which yielded about 12,000,000 gallons of refined oil, besides naphtha, solid paraffin, and other chemical products. This industry in Scotland is situate in four geographical divisions—1, Mid Lothian and Linlithgowshire; 2, Lanarkshire; 3, Fifeshire; and 4, Ayrshire. The largest works are to be found in the first of these divisions; among them are YOUNG'S Mineral Oil Company's works at Addiewell and Bathgate; the works of Messrs. Meldrum, Simpson, and M'Lagan at Uphall; the Mid Calder Company's Works at Oakbank; the West Calder Company's, the Glasgow Oil Company's, and the Bathville Works. In the Lanarkshire district there are the North British Oil Company's Works at Lanark, the Uddingston Works, the Coatbridge Works, and others of less note. The works in Ayrshire and Fifeshire are chiefly of limited extent, and manufacture only the crude oil. Altogether there are sixty-eight oil works in Scotland; at eighteen the crude oil is manufactured and refined, ready for market; at forty others the crude oil alone is made. The great bulk of crude oil is refined at other works in Scotland; but quantities are occasionally sent to the Welsh refineries and to the Continent.

The Addiewell Chemical Works occupy about 70 acres of ground, fully one-third of which area is covered by buildings, tanks, condensers, &c., while a large proportion of the remainder is taken up by railways, roads, and cask depôts, connected with so vast an establishment. The diversity of the operations connected with the works gives a corresponding variety to the buildings and iron structures which cover the ground, making them resemble a congeries of factories for very different purposes. The retort sheds taken together are upwards of 250 yards in length, and each contains a double row of retorts, numbering about 354 specimens in all. The main pipe which collects the vapour from the retorts and conducts it to the condensers is nearly a yard in diameter. The weekly consumption of shale at these works is about 3000 tons, the produce of 16 shale pits. The weekly yield of crude oil is about 115,000 gallons. About 50,000 gallons of burning oil, from 5000 to 10,000 gallons of lubricating oil, about 20 tons of refined paraffin, and 12 tons of sulphate of ammonia, are turned out weekly. The total number of workpeople employed at Addiewell is 1600, of whom 850 are shale miners. The aggregate number of persons in the employment of the company at these works is 3500. The wages paid by the company is about £100,000 a year. The Bathgate Works of the same company have in operation 240 retorts, and consume 2500 tons of shale per week.

At Leeswood, in Flintshire, the manufacture of paraffin and paraffin oils has been successfully carried on for some time. Here three varieties of material were used, severally named "the curly cannel," "the smooth cannel," and the bottom shale or "bastard cannel." It was not till 1861–62 that their suitability for the production of paraffin came to be known, and that chiefly through the efforts of W. C. H. JONES. The success attending the experimental trials led to the formation of the Leeswood Green Cannel and Gas Coal Company, and the oil works of Messrs. FERNIE & Co. at Leeswood, in Flintshire, and at Saltney, in Cheshire. The Leeswood cannel seam, now about exhausted, was about from 5 to 6 feet thick and of a limited basin-shaped area, which thinned at the boundaries. The upper portion of the seam consisted of smooth

cannel, of a thickness from 25 to 30 inches; below this lay the curly cannel, about 18 inches, and under this again the shale, ranging from 14 inches to 2 feet. The curly cannel yielded, on distillation, about 30 per cent of crude oil of specific gravity from ·875 to ·890; smooth cannel about 16 per cent., and a specific gravity from ·925 to ·940; and the shale, which was very variable, from 12 to 15 per cent. of crude oil, with specific gravity about ·900.

The North Wales and Cheshire, or Wold district, oil works have, from a threatened exhaustion of their supply of coal or shale for oil-making, been of late in a rather unpromising condition. The Leeswood cannel is said to have about given out, and considerable quantities of crude oil are sent from Scotland to keep the refineries there in operation. There are also a few works of this kind in Lancashire and Staffordshire. In France there are a few shale oil works in operation; but although bituminous shales of good quality exist in that country, they have not as yet been much utilized. In Germany this industry of oil-making has received considerable development, and there are many small refineries both for oil and solid paraffin; but the German trade is generally in a depressed condition, chiefly from the competition of American petroleum. In Russia a number of refineries already exist, and active measures are being taken to develop the enormous resources of that country in this branch of industry.

In New South Wales, at Hartley, near Sydney, a seam of coal has been found 5½ feet in thickness. This is one of the richest oil-producing coals yet discovered, equal to, if not surpassing, the Boghead and New Brunswick coals. In colour it varies from a brown to a brownish-black; when cut with a knife, or scratched with a sharp instrument, it exhibits a light-brown streak. When broken it shows a conchoidal fracture, and small streaks of a jet-like substance are found throughout the seam. As is usual in such cases, different portions of the seam vary in their yield of crude oil. Some portions give as much as 150 gallons per ton of coal, but the average may be taken at 100 gallons. William Jolly, of Sydney, first called attention to this valuable seam; and owing to his exertions a company has been formed—the Western Kerosene Oil Company—and works erected at Waterloo, near Sydney. After overcoming many difficulties, such as are usually met with in starting a new industry in a new country, W. Jolly had, in 1872, the satisfaction of seeing his works turn out about 6000 gallons of excellent burning oil weekly, besides other products in the usual proportion. From the samples of the heavy or "blue" oil portion, which have come to this country, it is evident that very good solid paraffin, of high melting point (131° Fahr.), and excellent mineral lubricating oil of suitable gravity (·900) may be made from this oil. The burning oil produced is very good for colour and smell, and being of high firing point, is perfectly safe. There is no doubt that this oil and paraffin manufacture is here capable of vast development; the New South Wales Shale and Oil Company, who now work the property, are supplying 10,000 gallons of crude oil per week.

Peat has also been tried as a source of paraffin, but hitherto the yield obtained has been so small as to render the scheme a failure in a monetary sense. The Irish Peat Company in 1849 obtained from the distillation of peat—

Watery matters,	30·614
Tar,	2·392
Gases,	62·392
Ash,	4·197
	99·595

The watery matter and tar yielded—

Ammonia,	0·287
Acetic acid,	0·207
Naphtha,	0·140
Volatile products,	1·059
Paraffin,	0·125

So that 100,000 lbs. of peat would only yield 125 lbs. of paraffin. In Hanover the distillation was more successful, 100,000 lbs. of peat yielding 300 lbs. of paraffin. The fact that shale yields quantities so much greater, as well as other products of even more commercial value, has prevented, so far, a repetition of the experiment.

A good deal of paraffin is prepared from ozokerit, which may indeed, from the large proportion it contains, be considered as impure native paraffin. Ozokerit (earth wax) is found in small quantities at Binney Quarry, Linlithgowshire, also in Wales, and in coal mines near Newcastle. It is chiefly obtained, however, from Galicia (Austria), where it occurs in connection with petroleum springs in the blue clay of the miocene formation, principally in Borislav, near Drohobycz, and Dzwiniacz, near Stanistawow, at the northern foot of the Carpathian Mountains. In 1875, of some 20,000,000 kilos. (nearly 19,000 tons), upward of eight-ninths came from Borislav alone. The native ozokerit is transparent, of pure honey-yellow colour, about as hard as common beeswax. It is sometimes found in lumps or layers from 1 to 3 feet thick, a lump sometimes weighing several cwts. More frequently, however, it occurs in thin layers and small pieces, which must be separated from the matrix; the smallest pieces are only obtained by a process of washing. The poorer qualities, which are coloured black, and are either too soft from abundance of petroleum, or too hard (asphalt-like in character), are mainly used for the production of paraffin. The best yellow "earth wax" is used for the manufacture of "ceresine," a factitious "white wax," which is exported largely to Russia to be sold as beeswax. In making paraffin from ozokerit, the crude hydrocarbon is first melted and drawn off; the residue boiled with water, to the surface of which any remaining ozokerit rises; the whole allowed to stand for several hours for any suspended impurities to settle out, and the hydrocarbon poured into moulds, which contain 100 to 120 lbs. It is shipped without further packing to England, Moravia, and Vienna, where

it is purified and converted into illuminating oils and paraffin.

The manufacture of paraffin is effected by distillation over direct fire, from iron flat-bottomed retorts holding 1500 to 2000 lbs., the products of such working being—

	Per Cent.
Benzine,	2 to 8
Naphtha,	15 to 20
Paraffin,	36 to 50
Heavy lubricating oils,	15 to 20
Coke,	10 to 20

The paraffin is pressed, treated with sulphuric acid and caustic soda, filtered through paper and fine animal charcoal, and manufactured into candles (GRABOWSKY).

The yield of crude oils and paraffin from coal, shale, bitumen, &c., will of course differ somewhat according to the temperature employed, form of retorts, and other circumstances. The following table, given on GESNER'S authority, may be taken as approximately accurate:—

Locality.	Volatile Matters Per Cent.	Coke Per Cent.	Yield of Crude Oil Per Ton.
ENGLAND.			Gallons.
Derbyshire,	48·36	53	82
Wigan (cannel),	44	56	74
Liverpool "	39	61	50
Poole (shale),	42	58	50
Newcastle,	35	65	48
SCOTLAND.			
Boghead,	70·10	29·90	120
Scotch cannel,	38	62	40
Lesmahagow,	51	49	96
PROVINCIAL.			
Albert coal, New Brunswick,	61·05	30·65	110
Asphalt rock, "	43	57	64
Pictou (shale), Nova Scotia,	27	73	47
AMERICA.			
Breckenridge,	61·30	38·55	130
Ouachita river (Askansas),	60	40	64
Ritchie County, Virginia (bitumen),	—	—	170
Bitumen, Cuba,	71	29	120
" Trinidad,	38	52	70
" Canada,	70	30	118
Illinois (gas stone),	26	Limestne	18
California,	70	30	116

In Western Europe, and more especially in Great Britain, the paraffins and paraffin oils produced are almost exclusively manufactured by the distillation of coals or of bituminous schists or shales. The Boghead or Torbanehill coal, the mineral worked by YOUNG at the Bathgate Chemical Works, is now almost completely exhausted. The small amount of it still remaining is not now consumed in the production of paraffin, but from its high yield (15,000 cubic feet per ton) is exported for gas-making. The Scottish oil works are now chiefly supplied with the bituminous shales of various districts.

Properties of Paraffin.—This remarkable substance when pure is a solid of a faint bluish white colour, highly translucent. It is free from taste or odour, of specific gravity varying from 0·8236 to 0·940; having a melting point varying from 16° C. to 80° C.; it burns with a clear white flame, without smoke or residuum; it does not stain paper, is of nearly the same composition as olefiant gas, 85·7 C., 14·3 H. Paraffin begins to decompose when exposed to a temperature exceeding 280° Fahr. When submitted to dry distillation, a portion of the paraffin is decomposed into liquid hydrocarbons. It is a non-conductor of electricity. When two pieces of paraffin are sharply struck together they emit a sound resembling a metallic ring; the higher the melting point of the paraffin the sharper is this sound. The character of the fracture surface of a block of paraffin depends much on the fusing point of a given specimen, and on the manner, whether quick or slow, in which it has been cooled. Paraffin melting at from 90° Fahr. to 110° Fahr. exhibits a well-defined crystalline fracture; from 110° Fahr. to 120° Fahr. the crystals become much smaller and less marked; and from 120° Fahr. upwards the fracture is very close and fine in the grain. Paraffin melting at 150° Fahr. (65°·5 C.), however, shows quite a change, presenting on fracture brilliant, white, needle-like crystals of a silky lustre. That melting at 170° Fahr. resembles beeswax closely, but it is not conchoidal in fracture.

The specific gravity of paraffins increases with the rise in their fusing points. The following results, with paraffins from Boghead coal, were obtained by GALLETLY:—

Melting Points of Paraffin. Deg. Cen.	Deg. Fahr.	Specific Gravities.
32·0	(89·6)	·8236
39·0	(102·2)	·8480
40·5	(104·9)	·8520
53·3	(128)	·9110
53·3	(128)	·9090
58·0	(136·4)	·9243
59·0	(138·2)	·9248
80·0	(176)	·9400

The elementary composition of paraffin is essentially that of olefiant gas, as shown by the following table:—

	Paraffin from Boghead Coal. M. P., 80° C. Galletly.	Paraffin from Boghead Coal. M. P., 52° C. Anderson.	Paraffin from "Grey" Shale, Addiewell. M. P., 55° C. W. MacIvor.	Paraffin from Ozokerit. M. P., 63·88° C. W. MacIvor.	Paraffin from Wigan Coal. M. P., 50° C. W. MacIvor.	Paraffin from Chinese Wax. M. P. 58° C. Brodie.	Paraffin from Beeswax. M. P., 62° C. Brodie.	Olefiant Gas.
Carbon,	85·2	85·15	85·31	85·26	85·29	84·90	85·31	85·7
Hydrogen,	14·4	15·40	14·50	14·53	14·40	14·21	14·44	14·3

Paraffin is insoluble in water; it dissolves in ether readily; with facility in cold essential oils and warm fat oils; it is very soluble in mineral oils and naphthas, and in benzol. It is very sparingly soluble in boiling absolute alcohol. The solubilities of the paraffins obtained from any particular source appear

to decrease as their fusing points increase. The following table gives the solubility of various paraffins in benzol:—

Melting Point of Paraffin. Deg. Cen.	Deg. Fahr	Solubility in 100 C.C. C. 18° C.	
35·0	(95)	133·0	grammes.
49·6	(121·28)	6·0	"
52·8	(127·04)	4·7	"
65·5	(150)	1·4	"
80·0	(176)	0·1	"

Paraffin when in the melted state is rapidly acted upon by chlorine, the hydrogen being replaced by that element and hydrochloric acid evolved. At first it becomes a gummy-looking solid, afterwards a liquid colourless and transparent, and as the passage of the chlorine is continued a hard brittle resin is the result. When paraffin of 130° Fahr. melting point (54°·44 C.) was employed, the specific gravity of the resinous body obtained was 1·603. It was of a pale lemon yellow colour, and exceedingly brittle; it decomposed on distillation, evolving large quantities of hydrochloric acid gas, with a small quantity of an oily distillate, a residue of carbon remaining in the retort. This resinous substance yielded as the mean of several analyses:—Carbon, 29·55 per cent.; hydrogen, 3·39 per cent.; chlorine, 66·82 per cent. Upon a paraffin melting at 80° C. (176° Fahr.) the action of chlorine is much more rapid; but otherwise the results are similar to those in the case of paraffins of lower fusing points.

Bromine acts on paraffin, replacing its hydrogen.

Gill and Mensel obtained cerotic acid amongst the products of the action of nitric acid on paraffin; more recently Pouchet describes ("Compt. Rend.," lxxix. 320) a yellowish, combustible, light, solid paraffinic acid, which he has obtained by similar treatment. It is crystalline, slightly soluble in alcohol, melts between 45° and 47° C., and has the formula, deduced from the analysis of the lead, barium, and silver salts, $C_{24}H_{48}O_2$. Nitro-compounds, as well as succinic and butyric acids, are also produced, the chief nitro-compound being of a clear, thick, oily nature, which is soluble in alkalies, and yields, on distillation, ammonia and pyridine bases. The most rapid action of nitric acid is upon paraffin melting at 80° C. Oxidation of paraffin is readily induced by the action of sulphuric acid and permanganate of potassium. When the two latter are heated together in a tube and a piece of paraffin dropped in, the action is so violent that often heat and light are evolved, sometimes accompanied by an explosion.

Sulphuric acid alone will attack paraffin if heated to a high temperature with it, and the more readily the higher the melting point of the paraffin employed. When paraffin and sulphur are heated together, the hydrogen of the paraffin unites with the sulphur, and sulphuretted hydrogen is evolved, carbon being separated; or if the paraffin be in large excess, a sufficiently steady and copious flow of the gas is obtained to render this a useful laboratory method of generating hydrogen sulphide.

At a considerable number of degrees below its melting point, paraffin becomes soft and plastic, and may be worked or moulded readily into any shape by the hand. For instance, paraffin fusing at 125° Fahr., which commercially is a good melting point, may be easily bent or twisted into any form at a temperature of 90° Fahr.

This property of paraffin is prejudicial to its employment in its pure state (that is to say, *unmixed* with other fatty substances), in the manufacture of candles destined for warm climates, or which may be long exposed in heated rooms, &c. The very high melting point of the paraffin obtained by refining some varieties of ozokerit seems, however, to a considerable extent to have overcome this difficulty. Candles of paraffin, with but a slight admixture of other material, may now be had for sale of a melting point of 140° Fahr.; and although not so free from colour as the candles made from the ordinary paraffin, they are not so apt to bend or gutter.

If paraffin, say of 125° or 128° melting point, be kept for a considerable time at a temperature between 90° and 100° Fahr., under a gentle pressure, a molecular change seems to take place; the paraffin from being simply *translucent* becomes perfectly *transparent*, like glass. Care must, however, be taken that the temperature of the paraffin is very gradually reduced to that of the surrounding atmosphere; in other words, the paraffin must be annealed to its new condition. A sudden knock or blow causes the piece of paraffin to resume its ordinary state.

When paraffins of different melting points are mixed together in various known proportions, the melting point of the mixture is as nearly as possible the mean of the melting points of the original paraffins employed.

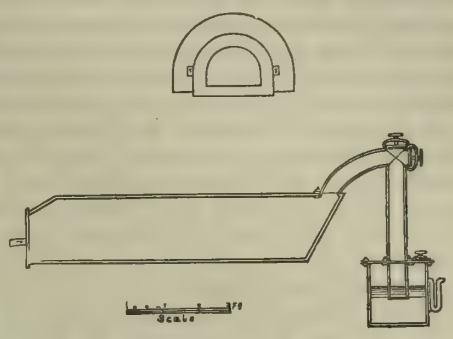
Paraffin mixes readily when fused with stearic acid, palmitic acid, beeswax, Japan wax, &c. It is found, however, that the melting point of such a mixture of fatty acid and paraffin is not the mean of the melting points of the constituents, as is the case when various paraffins are mixed together, but is uniformly lower than such a mean; and if the proportion of paraffin in the mixture be considerable, the melting point is frequently below that of either constituent separately:—Thus, Musselburgh Company's stearic acid, melting point 130° Fahr., was mixed in various proportions with Young's paraffin, of melting points respectively, 120° Fahr., 126° Fahr., and 127° Fahr.:—

Parts Musselburgh Co.'s Stearic Acid. Melting Point 130° Fahr.	Parts of Paraffin.	Melting Point Mixture with 120° Paraffin. Deg. Fahr.	Melting Point Mixture with 126° Paraffin. Deg. Fahr.	Melting Point Mixture with 127° Paraffin. Deg. Fahr.
55	45	114	113½	115½
60	40	119	116	118
65	35	121	118	120
70	30	122½	122½	122
75	25	124½	124	124
80	20	125¼	125½	125½
85	15	126	127	127
90	10	127½	128	129½
95	5	128½	129	130

The Manufacture.—The cannel or shale to be

operated upon, as it comes from the pit, consists of large irregular masses, which in the breaking shed are crushed by machinery into pieces small enough to be shovelled into the retorts. By crushing the materials are rendered loose and open in structure, so as to be more easily and rapidly penetrated by the heat. The cannel or shale so prepared is inclosed in suitable vessels, called retorts, and therein subjected to the degree of heat required to liberate and drive off their condensable vapours. These vapours are made to pass through an outlet on the distilling vessel, which again communicates with a proper condensing vessel. In the history of the oil and paraffin manufacture various forms of retorts have been suggested and tried; but only two sorts have been retained in extensive use, and these severally are known as *vertical* and *horizontal* retorts, depending on their position when in use. The vertical retort is generally in cross section an elliptical tube, which is also ellipsoidal in the bore, being widest in the middle and narrower at each end. It is about 12 feet long, and its greatest diameter is about 21 inches, and least about 14 inches. The upper end is capable of being closed by a hopper valve, counterpoised by a weight at the end of a lever. The retort is charged by a funnel-shaped opening, and the valve is luted by a little fine sand. The lower end of the retort is terminated by what is called the *nose piece*. This part dips into an iron trough containing water, which seals or lutes it. The trough is made with an incline sloping forwards, so as to admit of the convenient removal of the spent shale. A water-tap is attached to the trough, in order that the level of the water may be maintained. As the work goes on by means of a continually descending charge, the waste is gradually withdrawn and fresh coal or shale is added above. The portion of the retort which passes through the furnace is maintained at a dull red heat, and at this point the distillation takes place without interruption. The retorts used at the Addiewell Works are all of this description. The Bathgate old form of vertical retorts, at the works of Messrs. YOUNG & Co., was round in section, and ellipsoidal lengthwise. In diameter they were 14 inches, and each distilled a ton of shale every twenty-four hours. They were placed in sets of four each. At the larger and more recent works of the same company at Addiewell, the then manager, A. C. KIRK, suggested the introduction of elliptical retorts, in sets of six each, all heated by one fire. Each of these retorts can utilize 30 cwts. of shale in the twenty-four hours. At the Bathgate Works of this Company an intention to revert to the horizontal retort is now manifest, in substitution of the vertical form originally in use at the place. The distillation of cannels and shales in the production of oil appeared so like the process of distilling coals for the production of gas, that it was natural to suppose that the same sort of retorts should suit for both purposes. The ⌂-formed horizontal retort (Fig. 27) was therefore frequently adopted for oil distillation. This form when of large size, two or three being heated over one furnace, has proved satisfactory. The retorts are simple in construction, and readily charged and discharged. They may be made from 30 to 45 inches in width, and from 8 to 10 feet in length (GESNER). The latter size will distil three charges of cannel

Fig. 27.



coal of 450 lbs. each in twenty-four hours, at a heat not exceeding 780° Fahr. Forty or more of these retorts may discharge into one main, from which the gas is conveyed to a gasometer, to be afterwards used for fuel or for lighting.

It is necessary that the discharge pipes leading from these retorts to the main should not be less than 8 inches in diameter, to prevent pressure and insure safety; and they should be inserted into the end of the retort opposite the head and furnace, and upon a level with the upper part of the charge. The main itself should be 3 feet in diameter.

BRYAN JOHNSON, of Chester, has proposed another form of horizontal retort, differing from the former only in some details relating to the outlet and condenser. Most of these retorts are liable to the objection that the charge is heated only on one side, and the removal of the spent materials and recharge of the retort involve great labour and loss of heat and of condensable vapours. M. WILLIAMS, of Party Bodkin Works, Flintshire, devised a plan of retort wherein the charge was spread on trays, with a bottom of perforated iron. The heat is applied to the top as well as bottom of the retort, which vessel is 22 feet long and 3 feet wide; the layers placed on the trays are 6 inches deep. The constant difficulty of heating the charge throughout, or on all sides, and the large proportion of fuel used, are regarded as objections to this ingenious contrivance. Retorts of this kind are said to work the cannel slack most advantageously. Treated in the ordinary ⌂, the slack cakes and impedes the escape of the condensable vapours; when the mass is spread in layers this difficulty is very well got over, and greater productive power in the retort is the result.

An important improvement in the vertical retort was originated in 1873 by WILLIAM YOUNG, of Messrs. TAYLOR & Co's Works, by his invention of one in which the shale, after all the oily hydrocarbons have come over, may be used as fuel for heating up a fresh charge in the retort. This invention was so successful at the experimental works at Straiton that Messrs TAYLOR, as well as other firms

who have obtained the right from them, have brought this form of retort into very extensive use.

The following is a description of the experimental retorts at Straiton, abstracted from the *Oil Trade Review*, June 7, 1873:—

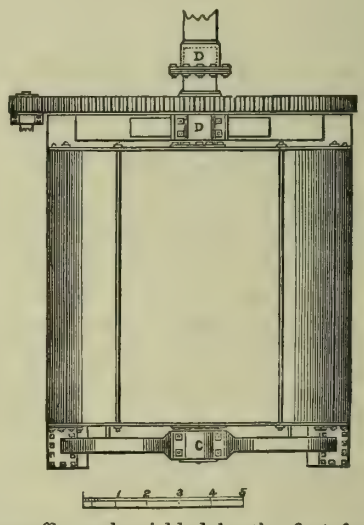
The experimental works consist of a stack of brickwork 10 feet square at the bottom, slightly tapering upwards, and containing four of the vertical retorts. These are of oval section, and slightly increasing in width from above downwards, being 15 feet in height, and the diameter 18 inches by 8 inches at top, and 26 inches by 16 inches at bottom. Each retort is cast in two pieces, though it is intended to have all subsequent retorts formed of a single casting: 10 inches is a sufficient thickness for the walls between the contiguous stacks or ovens, those for the outside being 20 inches thick. When the retorts are brought up to their ordinary working condition, the mode of procedure is to charge 5 cwts. at a time into each, the lower half containing an equal quantity, minus the volatile matters which have been distilled off; or, in other words, each retort is charged twice—its capacity being 10 cwts., and its working capacity twice that amount—in twenty-four hours. When a charge of 5 cwts. of shale is sufficiently distilled, the resulting coke is drawn into the combustion chamber underneath, where its hydrocarbonaceous contents are used in generating heat for the distillatory process. The combustion chambers are provided with fire-bars, ash-pits, and tightly fitting fire doors, and from them there are flues leading up into the retort-chamber, through which the heated gases have free circulation, the descending flue being in the middle of the chamber, and passing into an underground flue by which the products of combustion are readily conveyed away to the chimney stack. The aim of the working arrangements is, as nearly as possible, to have one-half of the contents of the retort in active distillation, while the other or lower half is nearly spent, and to have the coke of a spent charge at the same time undergoing combustion in the combustion chamber.

Though there is thus free communication between the combustion chamber and the interior of the retorts, a special arrangement is adopted to prevent the products of combustion from accompanying the distilled oils, and the heavier oil vapours from escaping into the combustion chamber, and so becoming wasted. The tube through which the vaporised hydrocarbons are drawn off is placed, as nearly as possible, at the junction of the two strata of shale, and by a suitable condenser the oil vapours are liquefied. The incondensable gas which accompanies them is returned to the retort stack, and is discharged into the retorts about 9 inches from the bottom, where it divides into two streams—one passing upwards through the bituminous shale to the outlets for the oil vapours, thereby removing such of them as might otherwise find their way to the combustion chambers, and the other passing downwards into these chambers to aid by its combustion in maintaining the heat necessary for the distillation. Thus the excess of gas is constantly disposed of, and the gas itself excludes the air from the retorts and prevents any deterioration of the oil from that cause. In order to induce free escape for the vapours from the retorts to the condenser, steam jet exhausts are used.

The advantages of this form of retort are various. At Straiton, for several weeks during which the retorts were in constant use, it was not necessary to use any coal, the permanent gas and the coked shale yielding a beautiful glowing heat in the combustion and retort chambers without more than the merest trace of smoke.

Then there is a decidedly greater yield of marketable products than with the ordinary vertical retorts. The Oakbank shale, which yielded in the old fashioned verticals at the Oakbank Oil Works 61·92 per cent. of finished products (burning oil, lubricating oil, and paraffin scale), gave, at the Straiton experimental works, 69·01 per cent., and one sample, distilled at a somewhat low temperature, 71·09 per cent.

Fig. 28.

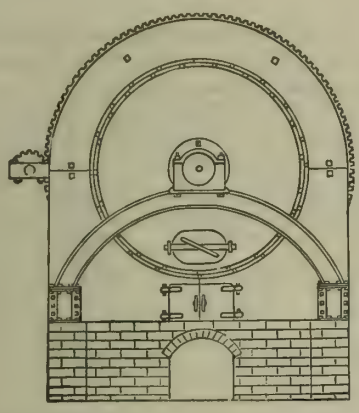


The paraffin scale yielded by the first form 8·12 per cent., and by the new form 11·76 per cent. The ammonia is also higher when the "self-heating" retort is used.

One important variety of retort is attributed to the Americans; it is known as the *revolving retort* (Fig. 28 represents a plan, and Fig. 29 a front elevation), and is intended to surmount a difficulty experienced in the use of other and prevailing forms of retorts, namely, that of subjecting the coal or shale under distillation to a uniform heat throughout. A, B, is the body of the retort, 7 feet diameter and 7 feet long, and of cast iron; cylindrical retorts of this kind have also been made of wrought iron. The cylinder turns on the axle, C, and D, D. The latter, D, D, is tubular, serving as a vapour outlet to the condenser, which again has a supplementary condenser connected with the first by a beak, with the view of arresting any condensable vapours that may have passed over from the larger one. The cylinder

or body of the retort is made to revolve by means of an endless screw, which acts on a toothed wheel mounted on the tubular axis of the retort. The charging door is at the end of the cylinder, and is

Fig. 29.



at the top when the charge is put in, being turned down to the bottom when the spent materials have to be withdrawn. As the cylinder revolves the charge within is turned over and over, bringing fresh portions of it continually into contact with the heated surface of the retort. The heat is communicated from the furnace by means of an arched flue. A very rapid and complete distillation is the result. These retorts are costly. They are liable to crack from unequal heating, and a lining of carbon deposit which takes place within them requires them to be cleaned out weekly; and the retort must be cooled for the purpose and heated up again, causing great labour and loss of fuel in the work. Cannel slack can be worked with advantage in these retorts. Caking coals are utterly unsuitable for them, and the dust caused internally by their revolution is apt to make very dirty crude oil.

The paramount object of the coal distiller is to obtain the exhaustive distillation of the coals with the smallest possible production of permanent gases. In consequence of the fact that the boiling point of the various hydrocarbons obtained differs so widely, it is impossible that all the lighter members shall escape before some have been decomposed into permanent gas by the heat necessary to distil over the heavier oils. Messrs. YOUNG at Addiewell obtain 3000 feet of excellent illuminating gas from every ton of shale distilled. Bathgate is supplied from the paraffin works, and the works at Addiewell are sufficient to entirely supply West Calder. At most crude oil works there is a sad waste of this valuable illuminant. Much difference of opinion is felt as to the relative values of the two forms of retort at present in use. A writer in the *Oil Trade Review*, speaking on this point, says: — "The Scotch oil makers are unanimous in favour of upright retorts, while the Welsh are equally unanimous in condemning them, and employing the horizontal. The probability seems to be, that the former are most useful in Scotland, whilst the horizontal suit the Welsh shale best.

"The ordinary Scotch shale being a bulky, cheap, and poor material, requires to be cheaply handled and rudely worked. So much shale has to be carried to the retorts and so much refuse removed from them for every ton of oil produced, that all the arrangements must be adapted for dealing with great bulk of raw material with the smallest expenditure of labour. The upright retorts can be arranged in long rows; a gallery, with a line of rails upon it, may thus be carried level with their mouths, and the shale shot down a funnel-shaped opening by mechanical devices similar to those used in charging a blast furnace. It gradually descends by its own gravitation to the lower opening, falls into a tank of water, from which the bulky and heavy residue is removed by means of trucks and rails similar to those used for charging. All this time the distillation goes on without stoppage. With horizontal retorts the charge has to be carefully put in and spread with a shovel or scoop, then the door luted on and screwed tight. When the distillation is completed, there is a halt in the operation; the hot door is unscrewed and taken down, set aside to have its old luting scraped off, the exhausted cannel or shale is raked out by hand labour and taken away—all in a bit-by-bit sort of fashion, involving a great deal more labour upon each ton of raw material than by the Scotch mode of working. On the other hand, the horizontal retorts do their work better; and where the raw material is of sufficient value to bear the extra labour, the increased and better yield more than covers the additional cost in wages."

In the vertical retorts the heat is applied from below, beginning from near the bottom, where it is most energetic; its direct action extends up to near two-thirds of the height of the vessel. The heat gradually diminishes upwards, and the liberated vapours force their way through the superincumbent mass of shale, till near the top of the retort they escape by a tube leading to the condenser. Behind each retort, and just above the junction of the nose piece with the retort, an inch pipe, fitted with a stopcock, is attached. This pipe is in connection with the main leading from the steam boilers. Steam, at a pressure of 10 lbs. per square inch, is passed by means of this pipe into the retort during the distillation. The steam sweeps the oil vapours out of the retort as fast as they are formed, and also, with the ascending condensable vapours and gases, tends to equalize the temperature of the mass of coal or shale under operation, rendering the heat more uniform throughout.

For every ton of shale distilled, a quantity of water, amounting to about 80 gallons, is thus in the form of steam passed through the retort. The water originally in the shale generally varies from 12 to 20 gallons, so that in vertical retorts worked in this way a total quantity of about 100 gallons of water is vaporized in the distillation of 1 ton of shale. The coal consumed in operating with the large oval

retorts, six in series, used at Addiewell, is much less than was formerly consumed by the small round retorts in sets of four. One ton of shale can be distilled in these oval retorts by the consumption of 3 cwts. of coal. At the back and top of each retort the vapour pipe passes on to the main leading to the condenser. A *bonnet* is attached to the vapour pipe, so as to admit of its being cleaned by means of an iron rod on the removal of the bonnet. This is required, as occasionally small pieces of solid matter lodge in the throat of the tube, obstructing the passage of the condensable vapours and gases. About 30 retorts is the proper number to have connected with one main; in some works, however, as many as 200 retorts are connected with the same main, whilst other makers advocate the use of special condensers for each set. At the end of the main, before it enters the condenser, a trap and separator are placed, so that all the products which have condensed in the main may be thence removed. The crude oil passes to one tank and the water to another tank called the *ammoniacal water tank*. The temperature in the main as it enters the condenser varies from 200° Fahr. to 210° Fahr. The pressure is very small, being not more than from three-fourths of an inch to 1¼ inch of water. These distinctions are of consequence to note in practical operations.

Comparison of the Yields of Crude Oil by Vertical and Horizontal Retorts.—The following results were obtained by experiments on the large scale; separate sets of vertical and horizontal retorts being detailed for the purpose, in order to make the results commensurate. The shale operated upon was the thick shale of the West Calder district. This is one of the principal shales worked by Young & Co., by the West Calder Oil Company, and others in their neighbourhood. Oval vertical retorts, with steam passed through during distillation, yielded 39·88 gallons of crude oil per ton, of specific gravity ·899 at 60° Fahr.; horizontal retorts, in sets of three, *without* steam, yielded 34·63 gallons of crude oil per ton, of specific gravity ·865 at 60° Fahr., showing a difference of 5·25 gallons in favour of the vertical retorts. The oil of the horizontal retort was of lower specific gravity, having been partially re-distilled in the retort, whereas in the vertical retort the vapours are rapidly swept out by the steam as they are formed. The average quantity of shale put through the ordinary sizes of horizontals ranges from 7 cwts. to 10 cwts. per retort per twenty-four hours. Steam is not usually passed through these retorts during distillation, as most manufacturers who have to sell their crude oil prefer to have it as low in specific gravity as possible. In cases where steam is employed about 3 gallons more crude oil per ton of shale are obtained; the oil is a little heavier than that produced in horizontals without steam. There are some varieties of coal whose behaviour when exposed to the action of heat renders them unsuitable for distillation in the vertical or continuous retort: in such cases the horizontal is found very convenient. The Hartley coal, near Sydney, New South Wales, and the coal from St. John's, New Brunswick, are instances of such minerals.

In pursuance of this inquiry, the following table will show that the vertical retort is more for the advantage of the manufacturer than the horizontal one:—

COMPARISON OF THE COST OF MANUFACTURING CRUDE OIL BY MEANS OF HORIZONTAL AND VERTICAL RETORTS.

	£ s. d.	£ s. d.
Cost of horizontal retorts, complete, to consume 100 tons per day,	6525 0 0	
Do., vertical do.,	5432 0 0	
Difference in favour of vertical retorts,		1093 0 0
Working expenses 5 per cent. on capital sunk, but not allowing for deterioration—		
Horizontal retorts, per 100 tons,	12 17 6	
Vertical do.,	9 19 9	
Difference in favour of vertical retorts,		2 17 9
Depreciation of vertical retorts per cent. per annum,	12·45	
Do. of horizontal,	11·00	
Difference in favour of horizontal retorts,		1·45

Working expenses are thus made up—

	Horizontal.	Vertical.
Drawing, charging, firing, and fitting,	1·000	·500
Disposing of refuse,	·500	·417
Coals for fire,	·800	·800
Repairs,	·060	·100
Interest on capital,	·216	·181
Shillings and decimals per ton,	2·576	1·998
Equal to, per 100 tons,	£12 17 6	£9 19 9

In foregoing there is not included breaking, laying down the shale, and foremen's wages, being equal in both cases.

Vertical retorts, assumed to yield 31 gallons, ·883 specific gravity—

	£ s. d.
100 tons shale, at 6*s.* laid down,	30 0 0
Working expenses,	9 19 9
3100 gallons at 3·095*d.* each,	39 19 9

Horizontals, yielding 26 gallons, ·846 specific gravity—

	£ s. d.
100 tons shale as above,	£30 0 0
Working expenses,	12 17 6
2600 gallons at 3·955d. each,	42 17 6

Depreciation as above (vertical), ·174 per gallon.
" " (horizontal), ·221 "

Laboratory examinations gave per 100 gallons of crude—

Horizontal.		£ s. d.
10 gallons naphtha, at 8*d.*	=	0 6 8
53·35 gallons burning oil, at 1*s.*	=	2 13 4
9 gallons heavy oil, at 6*d.*	=	0 4 6
2·09 gallons scale paraffin, at 2*s.* 2*d.*	=	0 4 6
= 8·320*d.* per gallon,		3 9 0

Vertical.		
Naphtha, none separated.		
51·98 gallons burning oil, at 1*s.*	=	2 11 11¾
18 52 gallons heavy oil, at 6*d.*	=	0 6 9
3·52 gallons paraffin scale, at 2*s.* 2*d.*	=	0 7 7
= 7·954*d.* per gallon,		£3 6 3

We thus pay 86*d.* more for 100 gallons crude from horizontals, and get 37*d.* more for the products, leaving in favour of verticals 49*d.* per 100 gallons, or ½*d.* per gallon.

It is a common error in the construction given to the sets of vertical retorts, to put them into too close juxtaposition, to employ fires too energetic for the dimensions of the flues and ports provided for

the distribution of the heat and escape of the products of combustion. In consequence of this crowding and narrowness of space the retorts come to be locally heated, and at the points of the constant impact of the heat oxidised or burnt.

Several patents have been secured for the distillation of shale by the agency of superheated steam. James Young made an extensive series of experiments on a large scale, employing this means of distilling. The steam having passed through a superheater, constructed on the plan of that employed in the hot blast in ironworks, was passed through an intermittent retort, which held about 7 tons of shale. The whole apparatus was found to be easy of construction, and to be kept in repair at a very trifling cost.

In three experiments Young found that the coal consumed per ton of West Calder shale distilled was as follows:—

	Experiment 1.	Experiment 2.	Experiment 3.
	Cwts.	Cwts.	Cwts.
Superheater consumption,	3·09	3·44	3·14
Steam boiler "	4·60	5·77	4·91
Total coal consumed for each ton of shale distilled, ...	7·69	9·21	8·05

The total quantity of coal consumed in the process appears large; but if that process were fairly set working, and suitable means of utilizing the waste heat devised, the item of fuel might be much reduced in cost; whilst retort repairs, a formidable part of the expense of the distillation of coal or shale by prevailing methods, would be trifling. Besides, the qualities of the oil produced are much improved by this plan of operating by steam, and the quantity of solid paraffin considerably increased.

A mixture of carbonic oxide and nitrogen was employed experimentally by Young. This mixture was obtained by sending a blast of air from a centrifugal fan through a cupola furnace full of coke. The results were tolerably satisfactory, as far as distillation was concerned, and the probability is that the difficulties experienced would have been removed on further experiment. It was found, however, that a much greater degree of condensing power was in this case necessary than when steam was employed as the distilling agent. When steam is used its complete condensation is necessary, as it obstinately retains an important quantity of oil vapour diffused throughout; this difficulty is also encountered in employing the gases referred to, and other considerations on the score of economy interfere with their use.

In the case of the horizontal and other forms of retorts, wherein no steam is employed, the apparatus for condensation is usually very simple, generally consisting of a few lengths of pipe leading from the exit tube of the retort, dipping into a long cylindrical main into which all the retorts unite, and wherein the condensed products fall. Between each retort and this main a stop valve is generally placed, so as to shut off all connection whilst any retorts are being drawn, or other operation is being performed which necessitates the stoppage of the connection. After traversing the main the vapours are usually made to pass through several connected tiers of pipes, having a fall to the main, or the oil reservoir. In general the condensing arrangements adopted are of a very crude and primitive nature. At most of the crude oil works quantities varying from 1 to 2, or even 3 gallons, per ton of shale distilled are lost from imperfect condensation.

When vertical retorts with steam are used, the apparatus of condensation is necessarily more complex. As has already been stated, at the ends of the main, before the vapours enter the condenser, a trap and separator are situated, so that the products which have been already condensed in the main are at once removed to their respective tanks. The condensers are in general much the same as those employed in gas works. A series of cylindrical cast-iron chests, having a double row of faucets in their upper side, constitute the base of the condensers. A large condenser may have 12 or 14 such chests. A pipe conducts the products from each chest to its appropriate tank. A trap is placed on this pipe just as it leaves the bottom of each chest. This trap has a movable lid, so as to permit of the pipe being examined periodically, and the passage kept clear. In some cases the condenser pipes are for the first two or three rows of chests surrounded with a jacket or metallic casing or box, through which cold water is made to circulate. This of course greatly facilitates condensation. Towards the end of the series of pipes it is necessary to have available the means of occasionally passing a jet of steam through the condensing tubes, as in cold weather the pipes are frequently obstructed by masses of carbonate of ammonia, or other solid deposits. All the products of the first six or seven chests are usually run to a separator, and thence the crude oil to its tank, and the ammoniacal water to the vessel appropriated to its reception. In the case of a condenser consisting of twelve chests, the first seven of which ran their condensed products to one tank, the specific gravity of the oil in that tank averaged from ·890 to ·896 at 60° Fahr. In this instance the products of the remaining five chests were run to a separate tank. These products being the last to condense, were consequently the more volatile portions of the oil. The contents of this tank are termed crude naphtha. The specific gravity ranged between ·790 and ·805 at 60° Fahr. It is of great advantage to collect thus the more volatile portions at as early a stage as possible; as in refining the naphtha separately, a few extra precautions prevent considerable loss from evaporation. At Addiewell the gas in the third naphtha chest from the end of the condensers is usually as low in temperature as the external atmosphere. The pressure generally averages from one-fourth inch to one-half inch of water. But although the temperature is as low as can possibly be obtained in this form of apparatus long before the gas leaves the

condensers, still the gas goes away quite saturated with light oil vapour. An approximate idea of the quantity of oil which is thus being lost may be obtained in the following way:—An ordinary wet gas meter is obtained and connected, by means of a pipe, coupling screw, &c., to one of the gas pipes leaving the condensers; the connection should be such as may be readily detached, as the meter requires occasionally to be weighed. The meter is filled with partially-refined heavy oil, from which the solid paraffin has been extracted (the so-called blue oil of some makers); the meter is then weighed, the weight noted, the connection to the gas pipe completed, and the gas turned on to the meter. As the heavy oil becomes saturated with light oil, the specific gravity of the mixture becomes less, and the bulk of the oil increasing, overflows into a vessel placed so as to collect the surplus. When the index has shown that from 500 to 1000 cubic feet—depending upon the nature and quantity of liquids contained in it—have passed through, the experiment may be stopped, and the gain in oil weighed and measured. The fractional distillation of a quantity of the mixture will indicate the quantity of light oil obtained by the process.

Young devised a plan for carrying on this operation on the manufacturing scale. This is effected by passing the gas up a tall tower filled with coke, down which the heavy or blue oil is made to trickle. The oil is repeatedly pumped to the top of the tower, and trickles through the interstices of the coke over and over again, till such time as it is quite saturated with the light oil; it is then removed to a still, where, by means of steam heat, the light oil is distilled off. The heavy oil remaining in the still after the steaming operation has been completed passes through a cooler, and is again employed in washing the gas. Two stills are necessary, so that the operation may be continuous; whilst one still is employed steaming the oil, the other one is being put in readiness for the reception of the oil which is in the meantime being saturated in the coke tower. By this process from three-fourths to $1\frac{1}{4}$ gallon of light oil or naphtha per ton of shale distilled may be obtained, depending to some considerable extent on the season of the year, and the consequent greater or less efficiency of the other modes of condensation. The specific gravity of the crude light oil or naphtha thus obtained was between ·715 and ·735 at 60° Fahr.: but ·730 may be taken as an average. The coke obtained as a residue in the distillation of the crude oil is well suited for use in the tower, if care be taken that the harder varieties of it be selected only.

We may now make a *resumé* of the products we have obtained, and see what arrangements are made for their final disposal. We have—

1.	Crude oil of specific gravity, say ...	·890 to ·896
2.	" light oil " " ...	·790 to ·805
3.	" " " " ...	·730

A quantity of *uncondensable* gas, amounting to about 3000 cubic feet per ton of shale distilled, and a quantity of ammoniacal water, amounting, in the case of vertical retorts with steam, to from 80 to 100 gallons per ton of shale, are also obtained. In horizontal retorts, wherein no steam is employed, the water is reduced to about from 12 to 20 gallons per ton; the water in this latter instance being, of course proportionally richer in ammonia. As our concern is more particularly with the liquid hydrocarbon products, we may briefly dismiss the gas and ammoniacal water in a few words. The gas contains generally the ordinary constituents of coal gas; its impurities are much the same, chiefly being carbonic acid and sulphuretted hydrogen; sulphide of carbon is not present in such a great proportion as in coal gas as usually prepared. After purification, in most cases, the shale or coal gas thus produced is high in illuminating value. In the case of the Midlothian and Linlithgowshire shales the gas is equivalent to between 27 and 28 standard candles. The gas supplied for the illumination of the town of Bathgate by Young's Company, from their works in that neighbourhood, is of this character, and is found to be very satisfactory. At other works, when no such use can readily be found for this product, the gas is usually conducted to the steam-boiler furnaces, and there employed as fuel.

The ammoniacal water, when obtained from horizontal retorts wherein no steam is employed, is treated just as in gas works; but when verticals, with steam, are in use, the quantity of water being relatively so much greater in proportion to the ammonia present, other methods have sometimes to be adopted.

At Young's Works the ammonia stills are worked under a slight pressure, and the water is forced into the stills by means of a donkey pump. Two boilers are employed as stills; a constant feed and *blow-off* being the plan adopted. No. 1 still may be worked at, say, 10 pounds per square inch; No. 2 at from 6 to 8 pounds. The water pumped into No. 1 passes afterwards through No. 2 still, and thence the hot water, having had nearly all its free ammonia removed, goes as feed for the boilers employed to generate steam to pass through the retorts. The vapours from both stills simply pass into a *cracker* box lined with lead, containing the sulphuric acid.

When saturated and *salted up* the crystals are removed to a sloping board to drain; the mother liquor being mixed with the sulphuric acid in the next batch. The sulphuric acid is usually employed about 1·74 specific gravity, but this is occasionally raised as may be found necessary; as, for instance, when *salting up* does not take place.

Oil of vitriol made from sulphur ought to be employed; that manufactured from pyrites, from the presence of iron and other impurities, being injurious to the colour and purity of the salt. The quantity of sulphate of ammonia obtained varies with the shale employed, some shales and coals yielding very much more than others. The shales worked by Young's Company at Addiewell and Bathgate yield about 9 pounds of sulphate of ammonia per ton. At Oakbank a greater quantity is obtained. The difficulties at first to be overcome

in the extraction of the ammonia from the weak water of the vertical retorts were considerable. The successful carrying out of the process described above is due to the exertions at Addiewell of James Young, jun., and John Calderwood.

The Refining of the Oils.—The process for the refining of the oils distilled from shale is almost exactly similar to that employed in purifying crude petroleum; and the stills, agitators, and condensers being in the two operations so exactly alike, we refer to that heading for a more detailed description of those pieces of apparatus.

The lighter oils—the naphtha and coke-tower naphtha—are treated with sulphuric acid and caustic soda, and submitted to distillation in stills employing a current of steam. This operation is repeated if necessary. The product has, when prepared from the coke-tower naphtha, a specific gravity of about ·720, the whole naphtha yield varying from ·740 to ·770. It is mainly used for burning in out-door flame lamps, as a substitute for turpentine in mixing paints, and as a solvent in various manufacturing operations, such as india-rubber working, the lighter varieties being burned in sponge lamps.

The crude burning oil, which varies usually in specific gravity from ·890 to ·896 at 60° Fahr., is passed into stills of malleable or cast iron, the former preferably, which range in size in the Scotch oil works from 600 to 2200 gallons. The distillation is carried to dryness—that is, until the residue in the still is in the state of coke. This coke is exceedingly porous, and contains hardly any ash; it is therefore employed in most works as fuel. It furnishes the best fuel for locomotive furnaces, as from its freedom from ash it does not close up the tubes of the boiler, as coal or ordinary coke does. But a more important use has been found for this substance. A company in Glasgow purchases it from the oil makers; more completely cokes it—that is, they drive off the traces of pitchy matter with which it is generally more or less contaminated—and afterward reduce it to an impalpable powder; in this state it is sold to iron founders as "blacking," and is by them employed to dust over their moulds before casting. Purchased at the oil works for 15*s.* a ton, it realizes £4 to £5 per ton when thus prepared for the iron founder.

The still is usually fitted with a worm-pipe condenser. In some cases these are collected together in one large water pond or tank, but the better form of construction is that of a separate condenser for each still.

The loss on distillation of such oil as we have referred to should not exceed 5 per cent. by volume.

Steam is passed through the crude oil during the distillation, but generally only when the still is nearly *run off* and on *heavy oil*. The distillate of the crude oil may either, as is generally the case, be collected altogether into one tank, or may be fractionated so as to suit the subsequent arrangements for refining. For many reasons, it is advantageous to fractionate the distillate, each fraction then receiving just the treatment which it requires, neither more nor less. The solid paraffin is not thus exposed to deterioration by long heating, &c. But for the sake of simplicity in description, it may be as well to consider the distillate of the crude oil as one uniform mixture. This distillate is usually termed *once run* oil. In the case of vertical crude oil of ·890 specific gravity, the total mixture of once run oil has a specific gravity of from ·860 to ·865. The once run oil is now subjected to agitation with sulphuric acid. This operation is performed in iron vessels of flat cylindrical form, when possible lined with lead; each vessel is fitted with a centrifugal stirrer, which acts much like a pump, and keeps up a constant and violent agitation in the contents of the vessel. The form of stirrer most approved of is that designed by A. C. Kirk. It is most effectual in its action; a stirring vessel, containing 2000 to 4000 gallons of oil, may be thoroughly and effectively agitated in the short space of seven minutes. It is of advantage to be able to agitate considerable quantities of oil at once, as thereby a better average mixture of the oil is obtained. In treating once run oil, the acid is sometimes given in two or three doses or stirs; some consider this plan better than giving the acid in one dose and stir. About 4 per cent. by volume of acid is usually given to the once run oil. The dirty acid, or acid tar, from the subsequent stirrings of the more refined oils, is usually here used instead of fresh acid; when enough tar is not to be had, it is supplemented by fresh acid of specific gravity of about 1·74—the *brown* or pan acid of the makers. After agitation, the contents of the vessel are run down into a settling tank, where the oil is allowed to settle. By means of a valve at the bottom of this tank the deposited tar is run off periodically, say at intervals of every five hours, till the oil is completely settled. This operation may take from six to twelve hours, depending greatly on the nature of the oil under treatment.

A great improvement in this part of the process has been effected by the new settling apparatus of Messrs. Galletly and MacIvor, whereby the acid tar is very rapidly removed from contact with the oil after the stirring operation has been completed. This apparatus will be attended to further on, in treating of the refined oils. The once run oil, after being settled from the acid tar, is now pumped to another agitating vessel, wherein it receives a treatment with about 2 per cent. of solution of caustic soda, of specific gravity about 68° Twaddell. After this stirring the oil is run down to a settling vessel, wherein it is allowed to separate from the caustic soda and impurities which it has brought down. After settling several hours the oil is usually pumped to a *charging* or *feeding* tank, placed at a sufficiently great elevation above the refinery stills or boilers, so as to admit of the stills being charged or fed by gravitation with the oil to be distilled. The stills usually employed in large works are of the form of boilers, cylindrical, of various sizes (some as large as 36 feet long by 7 feet 6 inches diameter); a very common size is 24 feet by 7 feet 6 inches diameter. They are usually flat ended, and are provided with

gauge cocks, gauge glasses, and safety valves similar to those fitted to an ordinary steam boiler. The safety valve is useful in giving warning in case of obstruction of the worm-pipe or condensing arrangement employed. The boiler is heated much in the same way as a steam boiler. Many have a fire-brick arch for some distance above the fire, in which pigeon holes are left, so as to distribute the heat more equally and prevent local heating, which is apt to injure the boiler. Each boiler is fitted with a valve at the further end of its bottom, by which the boiler may be run off or completely emptied when necessary. There are also man-hole doors, by which access may be had within when cleaning or repairs are necessary. Separate condensers, sometimes tiers of cast-iron pipes connected, and contained in a water tank, sometimes tubular, as shown in Fig. 21 (Petroleum), are attached to each boiler or still.

The total mixture of once run oil, after treatment with sulphuric acid and soda, as put into the boiler or still, has generally a specific gravity of about ·845. When the still begins to run slowly, steam is introduced. This brings away at first a great rush of light oil; the still is now run to the naphtha tank, till the specific gravity at the worm-end of the still is ·790 at 60° Fahr. From ·790, until solid paraffin makes itself apparent, the distillate is run to first stage burning oil tank. The still is fed during the distillation; that is, the oil is kept up to a certain point in the gauge-glass whilst the distillation is going on. The aim is to keep the specific gravity of the run of still as near that of first stage burning oil as possible. When the boiler or still has run its time, perhaps four or five shifts (forty-eight to sixty hours), it is now run down, as has been stated, when paraffin makes itself apparent; the products are shifted to the paraffin tank, and the still is run down till the oil is just about to leave the lowest gauge-cock in the still. The fire is now withdrawn, and the still allowed to cool a little. The contents of the boilers are run off by the cock at the back end of the boiler, and by gravitation pass to a still placed at a lower level (the still is of the form described in the distillation of the crude oil), when the contents are distilled off to dryness; the products of the distillation being transferred to the paraffin tank. This then describes generally the process as followed out in all the three distillations, the after treatment usually given to paraffin oil. In each of these distillations, by running the start of every boiler or still to the naphtha tank, till a gravity of ·790 is attained at the worm-end, the flash point of the finished burning oil will be found to be sufficiently high—generally about 120° Fahr. to 125° Fahr. in the close vessel.

The heavy oil obtained from the latter stages of distillation is found to contain large quantities of bright crystalline scales of solid paraffin in suspension; at least a second distillation is needed before these scales make their appearance. It would appear that the pitchy constituents which still cling to the paraffin particles hinder their crystallization. When in free suspension the paraffin readily assumes the crystalline form. The following are the solidifying temperatures of various solutions of paraffin in finished liquor:—

Containing lb. per Gallon.	Deg. Fahr.	Containing lbs. per Gallon.	Deg. Fahr.
·1	50	1·1	82
·2	56	1·2	85
·3	62	1·3	86
·4	72	1·4	88
·5	70	1·5	90
·6	73	1·6	97
·7	75	1·7	97
·8	76	1·8	101
·9	77	1·9	100
1 0	82	2·0	103

The solidifying temperatures given above were taken by melting the samples in their containing bottles, and then suspending them by a cord. On the first distinct indication of paraffin making its appearance the temperature was taken for each specimen.

The separation of brown paraffin scales is effected by bagging and pressing. The bagging is simply a filtration in canvas bags which are usually filled and tied up, then heaped together and thrown into perforated boxes till the greater portion of the oil filters out. The contents of the bags are then submitted to a gradually increasing hydraulic pressure, till the utmost degree of dryness is obtained in the cake of crystalline scales. The quantity of solid paraffin thus obtained depends on the low temperature at which these operations are conducted, as the oil is a solvent to the paraffin, and the quantity it is capable of dissolving rapidly increases as the temperature rises. The refrigerating machine of Kirk, used at Young & Co.'s Works, is found very effective at this stage of the manufacture. An improved form of a paraffin press operating on quantities of scales and oil, at a temperature of 30° Fahr., gave the following results of several experiments:—

1. Press filled with 105,000 grains, pressure of 83 lbs., continued for six hours.

2. Press filled with 50,400 grains; time taken, ten and a half hours.

The total oil pressed, 155,400 grains, yielding a total of 22,100 grains soft paraffin, from Bathgate finished liquor.

The paraffin scale which has been pressed from the heavy oil, and still contains much adhering oil and a considerable amount of colour, is mixed with some naphtha, cooled and subjected to heavy pressure. The oil and softer portions are dissolved out, and a smaller but purer cake of paraffin is taken from the press. This operation is repeated once or even twice if necessary. The loss of naphtha is considerable, and numerous patents have been taken out, some professing to effect the preliminary purification with a smaller waste of naphtha, and some to dispense with that hydrocarbon in the process altogether. A *resumé* of the most important of these will be found in a lecture by Frederick

FIELD, F.R.S., in the *Journal of the Society of Arts*, March, 1874, to which we are indebted for some particulars.

In MELDRUM's process (patent dated June 4, 1867, No. 1646) the impure solid paraffin is reduced to a powder, then sufficient naphtha is introduced to make it into a paste or pulp; after which the mass is subjected to pressure, or the solid impure paraffin and naphtha may be ground up together, and the mixture may be then subjected to pressure. The operation is repeated three or four times.

The purified cakes are melted in a still, through which free steam is violently passed, as well as confined steam, in a worm at about 25 lbs. pressure, in order to raise the temperature until every trace of naphtha has come away with the steam. The product from the still is mixed with from 3 to 5 per cent. of animal charcoal; heat is applied, and the charcoal allowed to settle.

Some finely divided particles which remain in the supernatant liquid are separated by filtration. The filter employed in the works of Messrs. YOUNG consists essentially of a jacketed case, kept hot by steam, and lined with a cylinder of wire-gauze, which is coated internally with flannel; and to make the filtration still more perfect filtering paper is introduced, so that the paraffin flows through absolutely free from solid particles, and if pure, as colourless as distilled water. This is run into cakes of various forms and sizes, generally in shallow oblong tins. Messrs. YOUNG & Co., however, prefer to form it into circular blocks, as being better adapted for transport in casks.

This spirit or naphtha process, combined with the use of animal charcoal, is a perfectly successful one, none more so; but it has the drawback that it is undoubtedly a dangerous process, and some manufacturers have with considerable success replaced this by other less dangerous processes.

JOHN FORDERD (patent No. 1858, year 1871) takes, say, 1 ton of crude paraffin, having, for example, a melting point of 120° Fahr., and melts it carefully in an iron tank, and allows the mechanical impurities, such as tar, sand, and the like, to fall to the bottom; after a few hours' repose he runs off the clarified paraffin into a number of hot metal trays, in which it solidifies into cakes, weighing about 10 lbs. each; these cakes are then placed edge to edge in a long bag of peculiar construction, and submitted to heat in a warm room, or in a bath of warm water till brought into a plastic condition. When this object has been attained, the bag of paraffin is submitted to the action of the kneading machine, which is supplied with a solution of soft soap in water, made in the following proportions:—Soft soap 10 parts, water 10 parts, previously heated to about 100° Fahr. This he calls the soap bath. On the machine being set in motion, the oil and colouring matter contained in the crude paraffin will rapidly combine with the soapy liquor, and form a temporary emulsion. He finds that any kind of soap soluble in water will answer for the above purpose; but he prefers to use the soft soap of commerce, and in the proportions named. He does not confine himself to the use of a bath of soap and water only, as he finds that various other liquors will act upon the paraffin whilst in a warm and plastic condition, such as solutions of the carbonated and caustic alkalies, mixtures of these with solutions of soap, a solution of rosin in alkali, the residual acid or alkaline liquor deposited from acidified hydrocarbon oils after washing or neutralization, and for some purposes, even warm water itself is sufficient.

A second patent, granted to R. M. LETCHFORD and W. B. NATION, No. 890, A.D. 1872, comprises, say the patentees, two objects; first, economy in the materials and labour employed; and secondly, the freedom from danger arising from the use of paraffin oil in the usual methods of refining. The process is conducted in the following manner:—

"We provide a tank, say about 12 feet by 6 feet and $2\frac{1}{2}$ feet deep, divided by cross partitions into V form cells $2\frac{1}{2}$ inches wide at the top and 2 inches at the bottom. The cells are open at the bottom, as the partitions stop short at 2 inches from the bottom of the tank; their upper ends are 9 inches from the top of the tank; there is a space of about 1 inch between cell and cell; there is a perforated lid or grating to fit into the tank resting on the top of the partitions. A grating with bars $1\frac{1}{2}$ inch apart is suitable. We fit steam pipes (free or closed) into the tank below the partitions. In using this apparatus we run water into the tank to the depth of 6 inches, and fill crude paraffin into the cells of the tank, and then secure the lid or grating to prevent the paraffin floating. We run more water into the tank to within 2 inches of the top, and turn on steam until the temperature of the water is within about 10° Fahr. of the setting point of the paraffin under manipulation; then we shut off the steam to allow the heat time to permeate the material. In about one hour we increase the temperature, raising it gradually for about four hours to within 2° of the setting point of the paraffin that was put into the tank; then we shut off the steam and take off the soft portions which have floated to the surface of the water. This being done, we run the water off to the top of the divisions, then melt the remaining paraffin in its cells, and let it stand to cool all night. In the morning the steam may be turned on again to repeat the operation, which is done as often as necessary to obtain the purity and hardness required. It is rarely necessary to do so more than four times; or the process may be conducted by first melting the paraffin in the cells and then cooling to 2° below the setting point of the material. We then secure the lid, add more water, and float out the soft portions. In either way we finally remove the lid, and take out the paraffin from which the low melting portions have been extracted; the low melting portions which have been removed are to be again treated like the crude.

"For obtaining fine degrees of whiteness, when the foregoing operations have been carried far enough,

we remove the clean paraffin to a steam-jacketed pan, adding thereto about 7 per cent. of commercial ivory black in powder, and keep it melted for four or five hours, until the whole of the ivory black is precipitated. We then cast into cakes in the usual way; the ivory black may afterwards be used advantageously in making blacking."

There is one more patent which may be mentioned (No. 3241, A.D. 1871, granted to Mr. Hodges):—

"The crude paraffin having, if desired, been first separated from rough impurities, is cast into cakes and allowed to cool slowly, so as to form into well-developed crystals. The cakes are then placed on a bed of absorbent or porous material, and are while thus placed exposed to a warm temperature, sufficient to render fluid the more easily melted portions with which the crystallized paraffin is mixed, but insufficient to melt the paraffin. The fluid and more easily melted portions then flow out from between the crystals of paraffin, and into, or into and through, the absorbent or absorbent and porous materials on which the cake rests. The cake—thus freed from the fluid, or fluid and more easily melted portions—may then be treated by any usual method to render it white, or as much lighter in colour as may be practicable; or the process may be repeated until the separation of the harder from the softer portions has been effected as completely as is desired, and then any requisite process for whitening the product may be adopted if needed."

It will be seen that all these processes have for their object the removal of the liquid from the solid hydrocarbons. The partially purified paraffin is by no means colourless, and still possesses considerable smell. In order to remove these objectionable qualities, it is melted by free steam, poured into a tank, and agitated by means of air with from 5 to 10 per cent. of strong sulphuric acid, arrangements having been made for the removal of the sulphurous acid generated. The agitation is continued for some hours, the length of time depending very much upon the nature of the paraffin. The acidified paraffin is, after drawing off, digested with heat with some bleaching agent, animal charcoal being most frequently employed. This digestion goes on for some hours, and then the charcoal is allowed to subside, and the liquid, if not quite bright, is passed through a filter kept warm by a steam-jacket.

In 1868 Messrs Fordred, Lambe, and Sterry took out a patent for the use of fuller's earth as a decoloriser of paraffin and other bodies.

"Twelve per cent. powdered fuller's earth is added to the melted paraffin, which is manufactured at a temperature of 230° Fahr., and well agitated, and after subsidence the clear paraffin is run off. We find that in all our processes, where we have mentioned fuller's earth as the agent to be employed, we can replace that substance in great part or wholly by marl clay, or other readily-attainable natural substance of like character. The fuller's earth, or analogous substances used in place thereof in any of the ways stated above, may be re-used, and the paraffin remaining adhered may finally be recovered from it by washing with agitation or other suitable means."

F. Field and Arthur Smith obtained a patent for employing artificial silicates instead of the natural ones such as fuller's earth. Most natural silicates are undecomposable even by strong acids, although certain silicates of lime or magnesia, or of both these bodies, are decomposed when the acids are concentrated, forming a gelatinous residue of silica and solutions of the bases. These gentlemen thought that by forming artificial silicates, and employing them, this decomposition might be effected, and the paraffin or other hydrocarbons separated by the addition of very weak acidulated matter. The artificial silicate found most applicable was the magnesium salt. The success of this process depends upon the purity of the salt, and the manner in which it is dried. Any soluble salt which accompanies its formation must be carefully washed out, and the gelatinous silicate dried at 212° Fahr., a heat higher than this greatly impairing its usefulness. An opalescent whiteness, freedom from smell, and a high melting point, are the commercial tests of good solid paraffin. Experiments have been made with a view to remove the opalescent whitish colour of solid paraffin, so as to render it perfectly transparent like glass. For this purpose prolonged and gradually increasing pressure has been tried, heating the specimen under operation at the same time. Sheets of transparent paraffin have been formed by this means, the plan being to reach transparency by hindering the process of crystallization from taking place in the substance as it solidified. Paraffin candles are now coming into extensive use by all classes of the community. This substance, besides being one of the most beautiful of chemical products, is chiefly recommended by being one of the most economical and brilliant illuminants. It is growing in popularity in households in town and country, and will keep that place in general estimation which it has won and continues to win.

The great bulk of the solid paraffin made is employed in the manufacture of candles (see Candle). A considerable quantity of the soft crude paraffin is employed instead of sulphur, for dipping the wooden splints for lucifer matches. Refined paraffin is used instead of wax in making tapers and the class of matches called Vestas, &c. Dr. Stenhouse has patented the application of paraffin to the waterproofing of cloth, alpaca, and other fabrics, and also as a means of preserving and waterproofing leather. It is found that paraffin greatly improves the finish of the finer class of woollen cloths, and for this purpose it is getting into exclusive use in the Leeds and Bradford wool districts. Paraffin has recently been applied to the preservation of animal food, butcher meat, fowls, &c. Under Professor Redwood's patent the food stuffs to be preserved were dipped into melted paraffin, kept at a pretty high temperature, from 300° to 400° Fahr. They thus receive a complete and impervious coating of solid paraffin. When it may be desired to use the meat or other article which has been so preserved, a plunge into

hot water at once removes the coating of paraffin, which in a melted state floats on the surface of the hot water. This process has not found much favour with the public. J. R. SCALLY, of Burton-on-Trent, has patented the employment of paraffin as a lining or coating for the inside of beer barrels, and for the water butts of vessels on long voyages. It has proved very successful for these purposes, inasmuch as bitter beer can now be exported to India in casks instead of bottles. When employed for a lining for the water casks of ships, it assists to keep the water quite sweet and wholesome for a long period. YOUNG'S Company manufacture a special quality of paraffin for these purposes; they term it brewers' paraffin. It is the hardest variety of the substance they are able to produce. It has a melting point of 134° Fahr. In cold alcohol paraffin of this melting point may be said to be almost insoluble, so that it is well fitted for the purposes contemplated by SCALLY'S patent. Paraffin is employed in frictional and voltaic electricity as an insulator, both alone and mixed with gutta-percha. For this purpose it is coming into various and important uses in the workshops of the telegraph instrument maker and the electric cable maker, and in the lecture room of the physicist. Paper saturated with paraffin is interposed as an insulator between the tin foil sheets in the condenser of the RUHMKORFF'S coil. In electro-deposition, in the operation of copying engravings on steel or copper, paraffin should prove of great utility. As a bath for the chemical laboratory, paraffin is an invaluable substitute for oil; for besides being much cleaner to handle, it may be heated to a higher degree than the oil used, without distillation or causing a disagreeable odour. Paraffin is being used by plasterers, instead of beeswax, for making the reverse moulds in which they cast their plastic. The iron founders of grates, fenders, and other ornamental articles, will find in paraffin an excellent substitute for the wax with which they take their first reverse moulds for their pattern goods. The artistic founders of statuettes and groups of minute figures in bronze or iron should find a similar use for paraffin. Attempts have been made to preserve ornamental stone work giving indications of decay, by means of a coating of paraffin. It has been found of use to the surgeon in treating cotton and linen cloth with paraffin for bandages for wounds. In the laundry paraffin is employed to give a high glaze to linens or collars when starched; it is for this purpose sold in cakes, under the name of *starch glaze*. Other and important uses will doubtless appear hereafter for this remarkable substance.

For further particulars relative to petroleum and paraffin the reader is referred to the pages of *The Oil Trade Review*; "The Journal of the Society of Arts;" *The American Chemist*; "The American Annual Encyclopædia" (APPLETON, New York), vol. for 1864; GESNER'S "Coal, Petroleum, and other Distilled Oils" (BAILLIÈRE BROTHERS, New York, 2nd edition, 1865); NORMAN TATE'S "Petroleum and its Products;" and to WATT'S "Dictionary of Chemistry," vol. iv.; to all of which sources we are indebted for valuable information.

PHOSPHORUS.—*Phosphore*, French; *phosphor*, German; *phosphorus*, Latin. Symbol, P.; atomic weight, 31.—This element abounds in nature, always in combination, and usually as phosphoric acid united to earthy and metallic bases. Phosphate of lime constitutes by far the greatest part of the hard matter of bones. It is also an ingredient of animal and vegetable fibrin and albumen. In the mineral kingdom, it is found principally as apatite, phosphorite, and staffelite.

Phosphorus was first obtained, in 1667, by BRANDT, a tradesman of Hamburg, while engaged in prosecuting researches upon urine.

In England ROBERT BOYLE, having seen phosphorus in the hands of KRAFT, of Dresden, who had purchased the secret from BRANDT, and knowing that it was extracted from the human body, commenced his investigations, which after a year's labour were crowned with success. In 1680 an account of the new substance was published in the "Philosophical Transactions," and it became known under the name of English phosphorus.

BRANDT and BOYLE evaporated urine to a thick creamy consistence. This was afterwards distilled, either *per se*, or after being mixed with sand or charcoal powder. In this process the carbon—either that which results from the charring of the organic matter contained in urine, or that which is added to it—decomposes the portion of the phosphoric acid which is in combination with ammonia, while that which is combined with the soda remains unaltered.

In 1769 GAHN prepared phosphorus from the bones of animals. The introduction of lucifer matches has enormously increased its consumption; indeed, at least 95 per cent. of the whole quantity produced is absorbed by this manufacture.

After the discovery of phosphoric acid in the bones of the vertebrata, the old methods of extracting phosphorus from urine were totally abandoned, and it is now obtained almost exclusively from bones.

Bone ash consists principally of tricalcic phosphate, $Ca_3P_2O_8$. This compound is not decomposed by ignition with charcoal, but the metaphosphate, which may be considered as tricalcic phosphate with phosphoric anhydride, is partially reduced:—

Calcium Metaphosphate.		Tricalcic Phosphate.		Phosphoric Anhydride.
$3CaP_2O_6$	=	$Ca_3P_2O_8$	+	$2P_2O_5$

In order to extract the phosphorus, calcium metaphosphate must therefore be produced. The bones are first thoroughly calcined with contact of the air, until the organic matter is entirely removed. The bone ash thus obtained is reduced to powder, and to every 3 parts are added 2 of concentrated sulphuric acid, and 16 or 18 parts of water. By this means the whole of the calcium carbonate of the bones is decomposed, and the tricalcic phosphate is converted into monocalcic phosphate (superphosphate), thus:—

Tricalcic Phosphate. Sulphuric Acid. Calcic Phosphate. Calcium Sulphate.

$$Ca_3P_2O_8 + 2H_2SO_4 = CaH_4P_2O_8 + 2CaSO_4$$

The monocalcic phosphate is dissolved and the calcium sulphate precipitates. After the separation of the sulphate by decantation and filtration, the phosphoric solution is concentrated by evaporation to a thick sirupy consistence. A quantity of charcoal powder, equal to one-fourth of its weight, is then added, and the pasty mass is exposed in an iron pan, with constant stirring, to a strong heat (nearly to redness) till perfectly dry. The water of the monocalcic phosphate is expelled, and a mixture of charcoal and calcic metaphosphate remains—

Monocalcic Phosphate. Calcic Metaphosphate.

$$CaH_4P_2O_8 = CaP_2O_6 + 2H_2O$$

The desiccated mass is then transferred to a stoneware or iron retort, connected by a wide elbow-shaped copper tube with a receiver containing water, into which the tube dips about a line. Another smaller tube, open at both ends, is attached to the receiver, to convey the uncondensed gases into the chimney. Heat is now applied, and is gradually increased to whiteness. The calcic metaphosphate, in contact with charcoal, is decomposed, the lime retaining only the quantity of phosphoric acid necessary to reconstitute bone earth (tricalcic phosphate). The excess of acid, and the water still remaining in the mass, are deoxidised by the charcoal, and the results are carbonic oxide and phosphorus. The phosphorus gradually rises in vapour, distils over, and is condensed in yellow drops in the water contained in the receiver, at the same time that the gases escape by the smaller tube into the chimney—

Calcic Metaphosphate. Tricalcic Phosphate.

$$3CaP_2O_6 + C_{10} = Ca_3P_2O_8 + 10CO + 4P$$

By mixing sand with the charcoal the whole of the phosphorus is obtained (Wöhler).

Calcic Metaphosphate.

$$2CaP_2O_6 + 2SiO_2 + C_{10} = 2CaSiO_3 + 10CO + 4P.$$

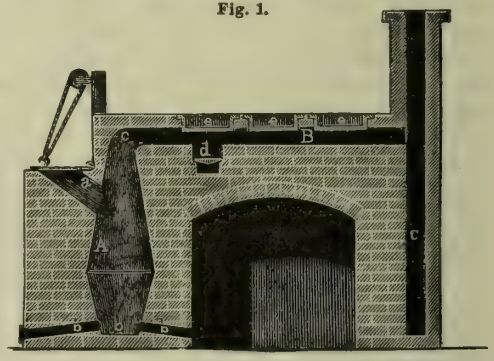
Preparation of the Bone Ash.—The bones usually employed in this manufacture are those of oxen, of sheep, or of horses. The bones of sheep are preferred, as the ash which they yield is less compact, and more easily attacked by an acid.

The process is conducted as follows, a reverberatory furnace being often used:—The fire is first well kindled; a quantity of bones are then introduced by the opening in the dome of the furnace. When these are well inflamed, a further supply is added until the furnace is about half filled. The operation now goes on of itself, and the combustion is very complete. When the combustion is ended, the ash is drawn out at the furnace door, and a fresh charge introduced at the upper opening. If, when the ash is drawn out, many black portions remain, these are returned to the kiln, and recalcined.

Very frequently bones are used in this manufacture from which the soluble gelatinous matter has been previously extracted. When these residues are collected in heaps, a rapid fermentation ensues, and they become heated and perfectly dried. They are afterwards burned in a reverberatory furnace, or one of similar construction. Before introducing the bones, the bed of the furnace is heated to redness. They are submitted to the action of the flame for the space of twenty hours, at the end of which time the incineration is usually complete.

A kiln designed and used by Fleck is shown in Fig. 1. A is the body of the kiln; *c*, the turret where the vapours are carried through the flue, B, into the shaft, C. A small furnace, *d*, is built in the bottom of the flue, so that the empyreumatic vapours are

Fig. 1.



perfectly consumed as they pass over the burning fuel. The bones are sent into the furnace through the opening, *a*, which is closed by a damper, and the ashes are withdrawn through the openings, *b b b*, on the hearth of the furnace. The pans, *e e e*, fixed in the upper part of the flue, are used for evaporating the liquors.

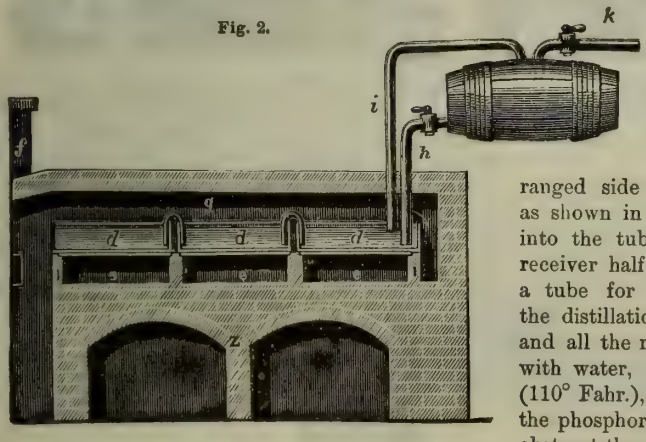
Second Operation.—The object of the next process in this manufacture is to transform the insoluble tricalcic phosphate into the soluble monocalcic phosphate (superphosphate). The operation is effected in a leaden cistern, or in a wooden tub lined with lead. To 3 parts by weight of the bone ash are added 2 of concentrated sulphuric acid, and from 15 to 20 parts of water, constantly stirring with a wooden spatula. A lively effervescence ensues, owing to the escape of carbonic acid. When this has subsided, the whole is transferred to a copper boiler, heated to the point of ebullition; and to promote decomposition, continued at this temperature for twenty-four hours. The liquid requires to be constantly agitated, to prevent the concretion of the mass. When completely decomposed, the mixture is suffered to remain at rest for ten hours, so that the sulphate of lime may subside. The supernatant liquid is afterwards drawn off by means of a leaden siphon, and conducted through leaden pipes to the filter, consisting of a conical linen bag of close texture, which retains the sulphate of lime, and allows the solution of monocalcic phosphate to pass through. The residue itself is then thrown upon the filter and strongly pressed, and afterwards thoroughly washed with successive portions of boil-

ing water. The filtrate is now concentrated, by evaporation in a boiler, to one-fourth of the original quantity, and again filtered to remove the portion of sulphate of lime which has become insoluble; the evaporation is then resumed till the liquid has a sirupy consistence. The mixture, which contains the soluble phosphate of lime, the excess of sulphuric acid, and a little sulphate of lime, is next gradually mixed with a quantity of powdered charcoal, about one-fourth of the original weight of the bones. The mass, after being evaporated to dryness, is further dried in a cast-iron kettle, at a nearly red heat, and with constant stirring with an iron spatula. During this process the greatest part of the water is disengaged; a portion of the excess of sulphuric acid is also set free; the remainder, by the action of the charcoal, is decomposed, and sulphurous and carbonic acids are liberated.

When hydrochloric acid is employed in decomposing the earthy phosphates, FLECK employs pans made of glazed stoneware or hard burnt earthenware for the evaporating vessels. These pans are about 3 feet square and 1 foot deep. They are made of pure clay, as free from lime as possible, and are glazed inside with a silicate similar in composition to blast-furnace slag.

The pans are placed about 4 inches above the bottom of the flue, *e e e* (Fig. 2), and are laid on metal plates or fire-brick walls, to protect them from the

Fig. 2.



direct action of the flame. The pans, *d d d*, are heated from above *g*, as well as below, and the vapours pass off along with the furnace gases to the chimney, *f*.

The pans are connected by siphons, and are filled or emptied in the following manner:—

A cask is placed with its bung-hole on the upper side, and an earthenware pipe, *h*, reaching from the head nearly to the bottom of the last pan. Two lead pipes are closely fitted into the bung-hole of the cask—one, *i*, passing into an earthenware pipe, which dips just below the surface of the liquor in the pan; while the other, *k*, is fitted with a cock, and communicates with the supply cistern. The cask is filled with liquor; the cock of the lead pipe is then shut, and the cock of the earthenware pipe is opened. The liquor runs off until the level reaches the open end of the pipe, *i*, which is then closed, and the flow of liquor is stopped. As the evaporation proceeds, the end of the pipe, *i*, becomes uncovered and admits the air, which displaces a fresh supply of liquor.

When the liquor has reached a density of 1·357 a crystalline crust is formed, which is broken, and the evaporation continued until a crystalline precipitate of the acid phosphate of lime begins to collect on the bottom of the pan. The contents are then siphoned off into a wooden cistern, where this crystalline deposit is rapidly formed as the liquor cools.

The mother liquor is concentrated in pans placed over fires, in order to obtain the remainder of the acid salt; and the mothers from this second operation are run into cisterns, treated with milk of lime, to recover the small quantity of phosphoric acid present, in the form of a basic phosphate, which is then acted on by hydrochloric acid as before.

The crystalline acid phosphate is then carefully drained to remove the chloride of calcium; and afterwards pressed to render it as dry as possible, on which point the larger or smaller yield of phosphorus greatly depends. The dry salt is then mixed with one-fourth of its weight of charcoal powder in an earthenware pan heated to 202° Fahr., and afterwards passed through a fine sieve, when it is ready for the retorts.

Distillation.—The perfectly dry mixture of acid phosphate of lime and charcoal is ground to fine powder in an iron mortar, and transferred as quickly as possible into the retorts. These, which are of earthenware, are arranged side by side in a reverberatory furnace, as shown in Fig. 3. The neck of the retort fits into the tubulure of an earthenware or copper receiver half filled with water, and furnished with a tube for the escape of the gas formed during the distillation. Each retort has its own receiver, and all the receivers are placed in a trough filled with water, at the temperature of about 43° C. (110° Fahr.), and kept at that temperature, so that the phosphorus distilling over may not solidify and obstruct the tubulure. In performing the distillation, a very high temperature is required. The furnace should therefore be sufficiently capacious to hold a body of fuel piled above the retort. Earthen-

Fig. 3.



ware retorts at a red heat become permeable to the vapour of phosphorus, and consequently require to be well and carefully luted externally. For this purpose a mortar, composed of clay and horse dung,

may be applied; or, still better, a mixture of freshly slaked lime and solution of borax. This mixture should be laid on with a brush in two or three successive coats, and forms an excellent vitrifiable lute. The copper tube opening into the receiver, and into which the beak of the retort is inserted, should be of considerable size, and so bent as to dip perpendicularly into the water, otherwise it will be apt to become plugged up by congealed phosphorus. It must also dip so little, that by no condensation could the water be forced back into the retort. The heat of the furnace in which the retorts are placed should be very slowly raised, allowing at least three hours to heat to redness; afterwards it is urged vigorously till all disengagement has ceased, the process requiring from fifteen to thirty hours, according to the size of the retorts. The disengagement of carbonic oxide continues during the progress of the operation; and when it has entirely ceased, the process is terminated. The proportion of the various ingredients used in the production of phosphorus is varied by different manufacturers.

The retorts used in Germany are sometimes worked in a similar manner to those used in gas-making (see Figs. 4, 5, and 6). Coal is employed as fuel. Each oven has five retorts heated by one fire, the flues (*b b b*) from which enter the same main flue, *e e*.

The retorts, *a*, are clay tubes open at one end, about 4 feet long and 10 inches in diameter. Each one is closed by a door, in the centre of which there is an opening into which a clay elbow pipe is fitted, which forms the communication with the receiver. The doors and pipes are all made fast with cement, and the retorts are coated on the outside with loam. The retorts are heated very gradually, and during

Fig. 4.

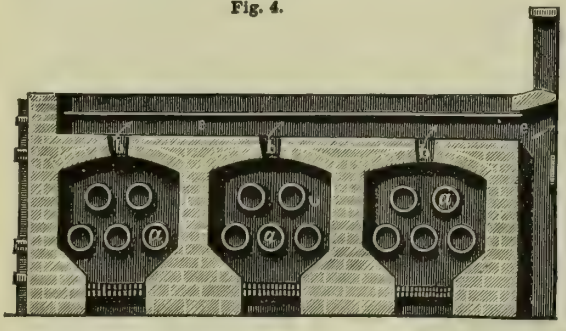


Fig. 5.

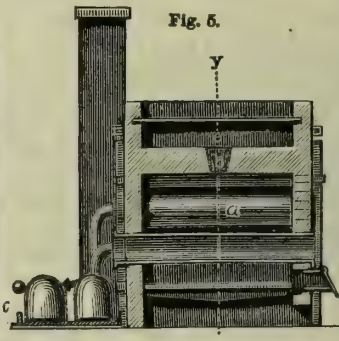
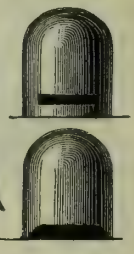


Fig. 6.



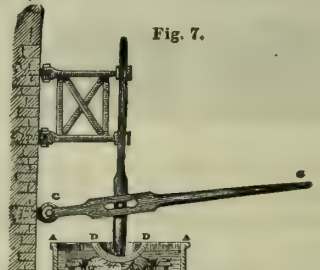
the preliminary firing they are charged with the mixture of charcoal and acid phosphate of lime, the produce of 3 cwts. of bones forming the charge for fifteen retorts.

The receivers consist of earthenware vessels of a muffle shape, open below, placed one behind the other in a tray (*c*, Fig. 5), through which a stream of water flows constantly. These muffles are about 3½ feet long, and have five openings on the top for the reception of the pipes from the retorts. The first is connected with the second by two pipes, and the latter has also two openings for the escape of the gases. The side of the muffle opposite to the stream of water has a narrow opening (*a*, Fig. 6), and the other side has a slit, *b*, about three-quarters of an inch from the bottom, to allow the water to escape, whilst the phosphorus is retained. The water runs into a cistern, where any phosphorus that may pass through the opening is collected. The pipes from the retorts penetrate about an inch into the receivers. By these arrangements the whole of the phosphorus vapour is condensed.

Purification.—The ordinary impurities are adhering charcoal, a reddish-brown phosphide of carbon formed during the process, and another reddish-looking substance, originally supposed to be an oxide of phosphorus, but ascertained by Schrötter to be phosphorus in an allotropic condition. Phosphorus, otherwise pure, generally contains a small quantity of this amorphous modification of the element. Arsenic is also frequently present.

Most of the impurities may be separated by simple fusion in hot water, and afterwards pressing through buckskin, or, still better, chamois leather. The operation is effected in the apparatus represented in Fig. 7. The phosphorus is first agglomerated by melting it in a water bath at 140° Fahr. (60° C.). When it has again solidified by cooling, it is wrapped in a perfectly clean and well-moistened chamois skin, C, which is then tied up, and immmediately plunged into

Fig. 7.



a copper colander, placed in the middle of another vessel, A, filled with water, heated to about 120° Fahr. (49° C.). When completely fused, the bag of skin is pressed upon by a wooden capsule, D D, by means of the lever, G G, increasing the pressure very gradually. The melted phosphorus passes through the pores of the skin, and collects in the liquid form at the bottom of the vessel.

Several other methods have been followed to effect the separation of the red amorphous phosphorus. It may be removed by digestion for a considerable time, and frequent agitation, in very dilute nitric acid, or in chlorine water, contained in a cask fitted with a gas delivering tube, which dips under water.

The redistillation of phosphorus is occasionally resorted to as a means of purification. On account of its excessive inflammability, the process demands great care and attention.

Recently French manufacturers have introduced a method of purifying phosphorus by passing it through coarsely-powdered charcoal, which is placed in a layer on a perforated plate in the vessel, A (Fig. 8), two-thirds filled with water, which is kept, by means of the water bath, B, at a temperature of 140° Fahr. (60° C). The molten phosphorus passes through the layer of charcoal, and is thereby purified. It flows through the open tap, C, and the tube, E, into the vessel, F (Fig. 9), filled with water, maintained, by means of the water bath, A, at a temperature sufficiently high to render the phosphorus fluid, so that it may, when aided by hydraulic pressure, pass through the perforated bottom, and the wash leather spread over it. The filtered phosphorus is then run off by the tap, G.

Fig. 8.

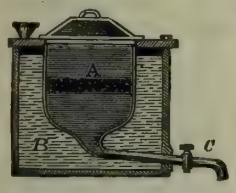
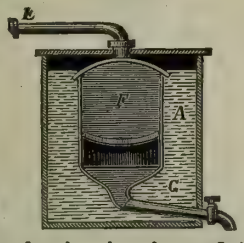


Fig. 9.

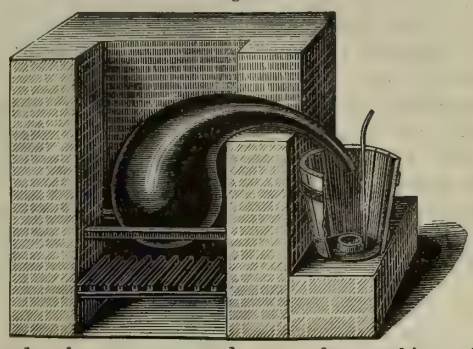


In another process of purification, porous, unglazed porcelain or earthenware pipes are fixed in an iron cylinder connected with a steam boiler. The steam forces the molten phosphorus (previously mixed with charcoal powder, for the purpose of preventing the pores of the plates from becoming choked) through the earthenware pipes. The charcoal remaining behind is used in the distillation of phosphorus. This method yields 95 per cent. of refined phosphorus upon the crude product.

In Germany phosphorus is purified by distillation, the operation being carried on in iron retorts of the shape depicted in Fig. 10. The neck of the retort dips into a basin filled to the brim with water. The crude phosphorus is fused under water, and mixed with 12 to 15 per cent. of moist sand. This mixture is then filled into the retorts. The object of mixing with sand is to prevent the phosphorus becoming ignited while filling the retorts. The yield of refined phosphorus is about 90 per cent.

In a phosphorus factory at Paris WAGNER states that the crude phosphorus is purified by mixing with it 3·5 per cent. of sulphuric acid and 3·5 per cent. of bichromate of potash; a slight effervescence ensues, and the result is that the phosphorus is

Fig. 10.



rendered very pure, and may, after washing with water, be at once cast into sticks. The yield is 96 per cent.

Moulding. — Phosphorus, as usually met with in commerce, is either in the form of round sticks, or granular. The moulding into sticks is effected by allowing it when fused to flow into glass tubes. A method frequently adopted is simply to plunge a slightly conical glass tube into the phosphorus melted under water, and causing it to ascend the tube by drawing out the air by suction with the mouth, being careful to have a layer of water between the phosphorus and the mouth. When the required quantity has entered the tube, the upper end of the latter is closed with the finger, and the whole is immediately transferred to a vessel filled with cold water. The removal of the phosphorus from the tube may be accomplished by gently pushing with a stout wire through the narrow end of the tube.

A very simple, and at the same time very efficient, mode of forming phosphorus into sticks, has been contrived by SCHUBERT. By the old system, the glass tubes, into which the phosphorus was poured to solidify, were frequently broken in forcing the phosphorus out by means of wires, and the method was, moreover, attended with great loss of time.

Fig. 11.

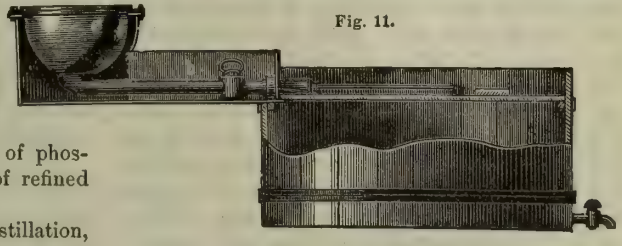
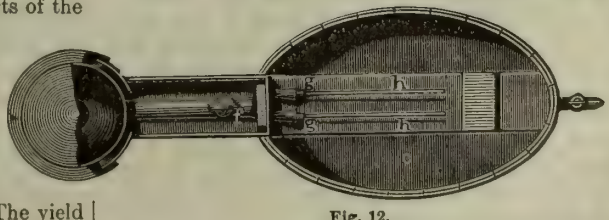


Fig. 12.



In Schubert's arrangement the melted phosphorus flows from a copper receiver, *e* (Fig. 11), through the pipe, *b*, into horizontal glass tubes, *g h* (Fig. 12), surrounded by water. By suddenly opening a stopcock, *f*, and again quickly closing it, a small quantity of phosphorus is allowed to pass through the glass tubes into cold water contained in a cistern, *c*, and in passing it closes the tubes, leaving a projecting rough piece of phosphorus which forms an excellent handle, whereby to draw the sticks from the tubes. The operation thus commenced, the cock is again opened, and the phosphorus drawn alternately from either tube, cut off with a pair of strong scissors, and allowed to fall into a cistern. By this method, from 15 to 20 lbs. of phosphorus may be formed into sticks in less than a quarter of an hour.

To obtain phosphorus in the granular condition, it is caused to fall in drops into cold water. Schubert's apparatus will also be useful in this operation. The cistern is filled to about three parts with cold water, and upon the surface of this is placed a layer of water heated to about 140° Fahr. (60° C.), high enough to cover the glass tubes which convey the phosphorus from the boiler. This is done by pouring the hot water upon a wooden trencher, swimming on the surface of the cold water. The difference in the density prevents the cold water mixing with that at a higher temperature. The stopcock of the vessel containing the melted phosphorus is slightly opened, so as to allow it to exude in drops. These, falling through the mass of cold water, become solid, and collect in the granular condition at the bottom of the cistern. Phosphorus may also be granulated by shaking it, while in the fused state, with a warm liquid, till it solidifies. Cassarca recommends for this purpose strong alcohol.

Properties.—Phosphorus at the ordinary temperature, when perfectly pure, is a soft solid substance, transparent and colourless. As generally found in commerce, it is of a light amber yellow colour, or even reddish, much resembling in appearance imperfectly bleached wax. After rapid cooling it is yellow, and semi-opaque like horn, and has a waxy lustre. At 32° (0° C.) it is brittle and crystalline in its fracture. The addition of an extremely small quantity of sulphur, even a $\frac{1}{300}$th part, is sufficient to render it brittle. Being totally insoluble in water, it is tasteless; its solutions in other liquids have, however, an acrid disagreeable taste. Neither has it any smell, though on exposure to the air it gives off vapours, which, undergoing a slow combustion, have an odour somewhat resembling that of garlic, or of impure hydrogen. Its specific gravity at 15° C. is 1·77. It melts at 44° C., and boils at 280° C.; forming a colourless vapour, the density of which is 4·35, air being unity. Phosphorus volatilizes at temperatures considerably below its boiling point, and in small quantities even at ordinary temperatures, as well *in vacuo* as in the open air. Several gases, as oxygen, hydrogen, carbonic acid, nitrogen, &c., when placed in contact with phosphorus, become charged with its vapour, and if boiled with water, it renders the aqueous vapour luminous.

Phosphorus is quite insoluble in water, but soluble—particularly if heated—in absolute alcohol, in chloroform, in fixed and volatile oils, and most of the liquid hydrocarbons, in chloride of sulphur, sulphide of phosphorus, and in ether. Its best solvent is, however, bisulphide of carbon, which dissolves one-fourth of its weight. Phosphorus crystallizes in regular octohedrons, and in rhomboidal dodecahedrons. Small dodecahedral crystals have been obtained by slowly cooling large masses of phosphorus. If a mixture of 2 parts of phosphorus and 1 of sulphur be melted under water, a compound is obtained, holding an excess of phosphorus in solution, and which is deposited in regular octohedral crystals on cooling. Its solution in sulphide of carbon, or in hot naphtha, when slowly evaporated in a current of carbonic acid gas, deposits regular dodecahedral crystals of considerable size.

When phosphorus is exposed to the air, even at ordinary temperatures, it undergoes a slow combustion, appears luminous, and diffuses white vapours possessing a peculiar penetrating alliaceous smell. The phosphorous oxide, P_2O_3, produced, attracting moisture from the air, condenses to a liquid, and, taking an additional quantity of oxygen, is converted into a mixture of phosphorous and phosphoric oxides, $P_2O_3 + P_2O_5$. This slow combustion is attended with a sensible evolution of heat, which gradually reaches the point at which phosphorus takes fire. It should therefore always be preserved under water.

The luminosity of phosphorus is so excellent a test of its presence, that if a drop of an extremely dilute solution of it in bisulphide of carbon be placed on a heated plate in the dark, the presence of $\frac{1}{12,000}$th part is readily detected.

Phosphorus reduces the compounds of the noble metals, when placed in contact with their solutions, and quickly becomes covered with the reduced and precipitated metal. In contact with chlorine, bromine, and iodine, phosphorus inflames spontaneously, and without the aid of heat, producing respectively, chloride, bromide, and iodide of phosphorus. When heated in a copious supply of dry air, phosphorus burns with a brilliant white light, producing white fumes of anhydrous phosphoric acid, P_2O_5, which, when condensed, much resembles snow.

White Phosphorus.—This amorphous modification is gradually produced whenever phosphorus under water is exposed to sunshine or ordinary daylight. The opaque crust is yellow at first, but afterwards turns white. Its specific gravity is 1·515. It smells like ordinary phosphorus, is luminous in the dark on exposure to the air, but turns red in daylight much more quickly than colourless phosphorus.

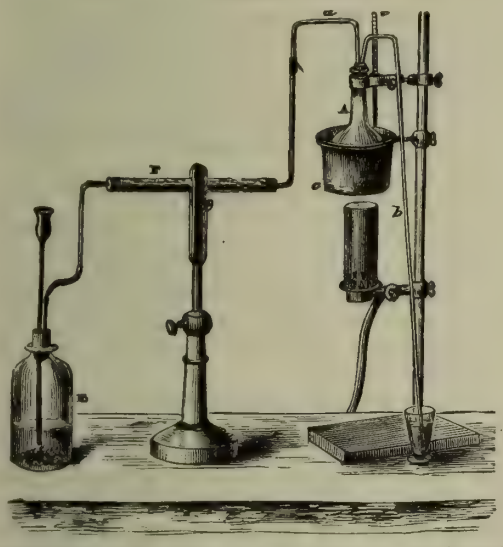
Liquid Phosphorus.—Phosphorus, under certain conditions, after having been fused, retains the liquid form for some time after cooling. This variety of phosphorus has the appearance of a transparent oily liquid. It may be obtained by fusing ordinary phosphorus with an aqueous solution of potassium hydrate.

Black Phosphorus.—Phosphorus is melted at 44° C., and while in a state of fusion is poured quickly

into very cold water. It is produced by the exposure of phosphorus to light in an atmosphere free from oxygen, or by heating it with a small quantity of iodine. The black colour disappears, and it is reconverted into the ordinary condition by remelting, and slowly cooling.

Red Phosphorus. — By far the most important allotropic modification of phosphorus is that known in commerce as the amorphous phosphorus of SCHRÖTTER, or *red phosphorus*. A quantity of dried phosphorus is placed in the flask, A (Fig. 13), to the neck of which a long narrow tube, *b*, bent downwards, is attached, the open end of which dips into a little mercury. The removal of the air from the flask is

Fig. 13.

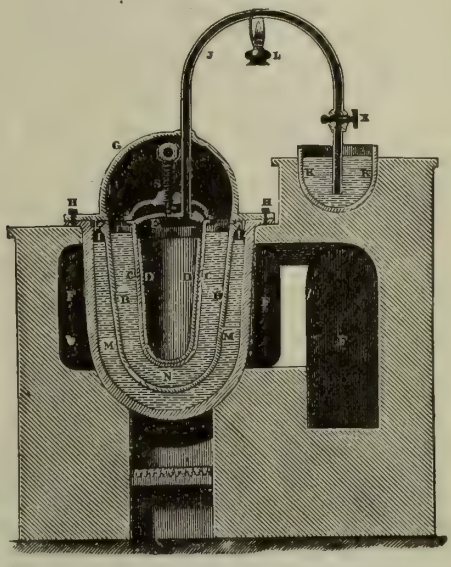


accomplished by means of a current of carbonic acid evolved from the bottle, E, containing marble and hydrochloric acid; the gas is dried by passing it over chloride of calcium, contained in the tube, F. The flask being emptied of air, the tube is closed by fusion at the narrow portion, *a*, and the apparatus evolving carbonic acid is detached. The flask is then heated by means of an oil bath, *c*; the phosphorus melts readily; and by regulating the heat steadily between 230° and 235° C., by means of a thermometer, *t*, and maintaining it thirty or forty hours, nearly the whole will be converted into the solid amorphous variety. When the metamorphosis appears to be complete, the apparatus is allowed to cool. Any unaltered phosphorus is separated by digestion in bisulphide of carbon, in which amorphous phosphorus is insoluble. The latter is afterwards collected on a filter, and washed with bisulphide of carbon as long as anything is removed from it, which may be ascertained by evaporating a small portion in a watch-glass, when any dissolved phosphorus will remain behind.

The red powder obtained by the above process, if not quite free from ordinary phosphorus, inflames spontaneously, but if quite pure suffers no alteration by exposure to the air. To effect complete purification it should be boiled in solution of potash of specific gravity 1·30, and then washed first with water slightly acidulated with nitric acid, and lastly with pure water. The colour of this amorphous phosphorus is deeper the higher the temperature at which the transformation is effected, and in that of the finest specimens is more brilliant than vermilion.

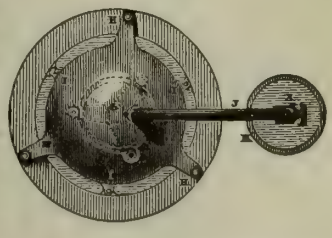
A vertical section of the apparatus employed by ARTHUR ALBRIGHT for the manufacture of red phosphorus is represented in Fig. 14, and a view of it, as seen from above, in Fig. 15. It is a cast-iron vessel set in brick-work, and having a fire-place underneath, with suitable flues, F F. From the inside

Fig. 14.



of the flange of this vessel, a similar vessel, B B, of the same material, is suspended, and secured by means of the screw-pins, I. The space between the two vessels contains a metallic bath, M, composed of a mixture of equal parts of tin and lead. G is a cast-iron cover to the inner vessel, B, fitting the upper edge by means of a groove, and fastened to the outer vessel by the screw-pins, H H. A screw, S, passes through a three-armed iron holder, which is attached to a third movable iron vessel, C C, placed in a sand-bath, N. In the interior of this iron vessel, C C, another vessel of glass or porcelain, D D, is fitted, in which the phosphorus to be operated upon is placed. J is a curved pipe of iron or copper, passing freely through the cover, G, but screwed into the cover, E, and having an exit at the extremity into a detached vessel, K K. This contains water or mercury; if the latter be employed, it should be

Fig. 15.



covered with water. The pipe, J, immersed in the mercury or water, serves as a safety valve, preventing the return of the atmospheric air into the inner vessel, C C. The spirit lamp, L, is placed under the pipe, J, and is used, if necessary, to heat the curve, and prevent condensation of gaseous phosphorus, which, if allowed, would obstruct the passage. The stopcock, X, is used to prevent the ingress into C C of the contents of K K, or of atmospheric air, and should be closed as soon as the operation is concluded, and before the apparatus in the furnace is allowed to become cool, or the vessel, K K, is removed. The cover, G, is not essentially necessary, its principal use being to prevent accidents. Between the end of the screw, S, and the cover, E, a small but strong concave disc or spring of steel is inserted, and so adjusted as to give a slight play to the cover, E, in case of violent action arising in the interior, or the stopping up of the pipe, J, by condensed phosphorus. The phosphorus to be converted into the amorphous state is previously melted and cooled under water, and afterwards dried as completely as possible. The mode of effecting the conversion is then as follows:—The phosphorus is deposited in the inner vessel, D D, and the covers, E and G, replaced. A fire is then kindled under the outer vessel, and the temperature raised to such a degree as shall be sufficient to drive off the air and other gases that may be generated in the interior vessel; these will escape at the exit of the pipe, J, which dips into the mercury or water contained in the vessel, K K. When mercury is employed it is desirable to cover it with a layer of water, so that any phosphorus which may distil over, and pass down the pipe, J, may be covered thereby. The temperature is now to be gradually increased until bubbles escape at the end of the pipe, J, which inflame spontaneously as they enter the air. When the gas has escaped freely for some time, the temperature may be further raised to 500° Fahr. To regulate the temperature, a thermometer is placed in the metallic bath before described. The length of time during which it is necessary to maintain the temperature, depends so much on accompanying circumstances that it can only be ascertained by experience. The heat should never be raised more than a few degrees above 500° Fahr. As soon as the operation is concluded the vessel is allowed to become cool. The phosphorus is then taken out, to effect which it may be necessary to break the glass or porcelain vessel containing it. Should it be desirable to increase the pressure on the vessels, C C and D D, the vessel, K K, holding the mercury may be deepened, that it may contain a greater quantity, and thus a pressure of an atmosphere, or even more, may be gained. In this case it will be necessary to remove the steel spring at the end of the screw, S, as soon as the steam and inflammable gases which arise in the first part of the process have ceased to issue from the pipe, J.

The phosphorus is then levigated under water, to remove any unconverted phosphorus, and drained by means of a bag or filter.

Red amorphous phosphorus in the state of powder is lustreless, and destitute of crystalline structure. Its colour varies from a scarlet to a carmine red; sometimes also to a blackish-brown tint. When in the form of coherent masses it is reddish-brown, exhibiting perfect metallic lustre and an iron-black fracture; sometimes the lumps are also of a bright scarlet colour; usually, however, dark reddish-brown. It is brittle, very fragile, with a perfect conchoidal fracture; specific gravity at 15° C. is 2·14. It is far less combustible than ordinary phosphorus, and is not luminous in the dark. When quite pure it will bear a tolerably high temperature without igniting. It is not altered by exposure to the air at the ordinary temperature; but if heated to 260° Fahr. in an inert gas, it passes into the state of ordinary phosphorus. Red phosphorus is insoluble in bisulphide of carbon, alcohol, ether, naphtha, chloride of phosphorus, and other solvents of ordinary phosphorus. In spirit of turpentine and other liquids which boil at a high temperature it dissolves very sparingly during ebullition, but is deposited on cooling as ordinary phosphorus.

Red phosphorus is perfectly free from those pernicious qualities which render the application of ordinary phosphorus so destructive to health. In a commercial point of view it is also advantageous, as the red variety may be transported with perfect safety, while the carriage of ordinary phosphorus is attended with considerable trouble and risk, and consequent expense.

Lucifer Matches.—Phosphorus is chiefly used for the manufacture of lucifer matches. Wood is cut into splints by machinery (sometimes by hand), and dipped in sulphur, paraffin, or stearin; and finally tipped with a combustible composition containing phosphorus, and some body which parts readily with oxygen. These materials are generally saltpetre, red lead, manganese; the whole being bound together with glue or gum.

The glue or gum is dissolved to a thin syrup, and is heated to 122° Fahr. (50° C.); the phosphorus is gradually added; and lastly, the other ingredients, after being finely powdered. The proportion of phosphorus varies, being sometimes as much as 30 to 50 per cent., and sometimes as low as 5 per cent. In sulphur matches the following compositions are used:—

Phosphorus,	4
Saltpetre,	16
Red lead,	3
Strong glue,	6

Another—

Phosphorus,	9
Saltpetre,	14
Manganese dioxide,	14
Gum,	16

Phosphorus is readily soluble in bisulphide of carbon, which, on evaporating, leaves it in a finely divided state. As the bisulphide is cheap, this method is used to introduce the phosphorus into the igniting composition without the use of heat, and at a considerable saving of phosphorus.

The mixtures used in the trade are kept secret. The following are given by WAGNER:—

I.

Phosphorus,	1·5	
Gum,	3·0	
Lamp black,	0·5	
Red lead,	5·0	A mixture technically known as oxidised red lead.
Nitric acid at 40° B.,	2·0	

(Specific gravity, 1·384).

II.

Phosphorus,	8	Dissolved in the required quantity of bisulphide of carbon.
Glue,	21	
Red lead,	24·4	
Nitrate of potash,	24·0	

III.

Phosphorus,	3·0
Gum,	3·0
Red lead,	2·0
Fine sand and smalt,	2·0

When the wood splints are coated at the ends with paraffin, stearin, &c., a larger amount of oxygen has to be supplied to cause ignition by friction; the mixture is then:—

I.

Phosphorus,	3·0
Strong glue,	3·5
Water,	3·0
Fine sand,	2·0
Vermilion or Prussian blue,	0·5
Chlorate of potash,	3·0

II.

Phosphorus,	3·0
Gum,	0·5
Water,	3·0
Fine sand,	2·0
Lead dioxide (oxidised red lead),	2·0

Wax matches are tipped with a mixture containing—

Phosphorus,	12
Gum,	14
Sulphide of antimony,	3
Lead dioxide (or Read lead, 35 / Nitric acid, 21 } 56)	36
Vermilion,	0·1

Safety Matches.—Matches made with amorphous phosphorus are difficult to ignite, and they have not come largely into use. The red phosphorus has, however, been found suitable for the manufacture of matches which shall only ignite when rubbed on a surface containing it.

The matches themselves contain no phosphorus; this is supplied by the surface on which they are to be rubbed. The idea first originated with BÖTTGER, and has since been improved on by LUNDSTRÖM, of Sweden, and COIGNET & Co., of Lyons. LUNDSTRÖM'S patent is worked in this country by BRYANT & MAY.

The paste is composed of:—

Chlorate of potassium,	6
Sulphide of antimony,	2 to 3
Glue (dry),	1

The paste for the rubber—

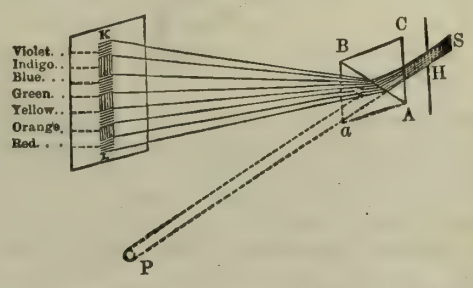
Amorphous phosphorus,	10
Manganese dioxide, or sulphide of antimony,	8
Glue (dry),	3 to 6

PHOTOGRAPHY.—By means of suitable lenses an image may be formed of any object. Photography is the art by means of which these images are rendered, to a certain extent, permanent.

The word photography is derived from two Greek words signifying to *delineate by light*. In point of fact, it is neither to the light nor to the heat of the solar rays we are indebted for the beautiful results of photography; but to a principle existing in combination with the light and heat of the sun, to which has been applied the name of *actinism*—a term derived from the Greek word for a *sunbeam*, and signifying merely the influence of the sun's rays, or *ray-power*, without involving the assumption of any theory on the subject.

To illustrate the composition and coloured refraction of the sun's rays: suppose a beam of solar light is admitted into a darkened room through an aperture, H, in a window shutter (Fig. 1), and that it is

Fig. 1.



made to pass through a prism of glass, A B C; instead of being refracted as a whole and appearing still as white light, which it does when the refracting surfaces are parallel, it is lengthened out and exhibits the well known solar spectrum, which is commonly divided arbitrarily into what are termed the seven prismatic colours—violet, indigo, blue, green, yellow, orange, red.

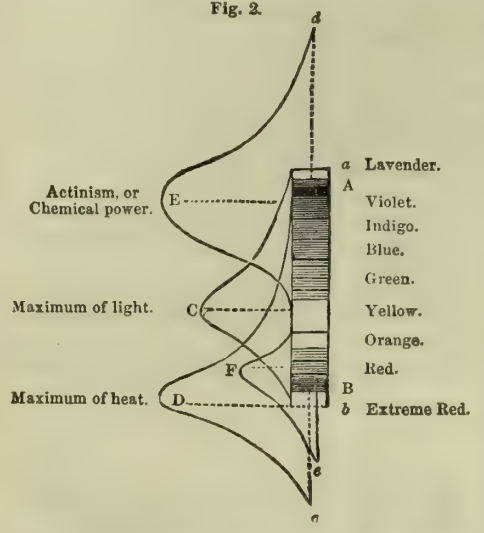
The order of succession is invariable, and depends upon the unequal refrangibility of the different coloured rays of which the white ray is made up. Thus the red ray deviates least from the direct path, S P; and the violet ray, most; and the intermediate rays have intermediate degrees of refrangibility: the orange is thrown further from the direct path than the red, and the indigo deviates less than the violet; hence the violet end is the most refrangible, and the red the least refrangible end of the spectrum.

It is important to remark, however, that below the ordinary visible red, or least refrangible ray, another ray of a deeper red, distinguished as the *extreme red* or *crimson ray*, may be detected by examining the prismatic spectrum through a deep blue glass; and by throwing the spectrum upon a piece of yellow paper, another ray appears at the violet extremity, named, by Sir JOHN HERSCHEL, the *lavender ray*.

Fig. 2 shows the spectrum. The curved lines in the engraving represent the relative amount of *actinism*, *light*, and *heat*, in different parts of the spectrum. It will be observed that the actinism is

greatest at E, and ceases at *d* and *e* towards either extremity. At the point of greatest light, C, which is in the yellow ray, there is absolutely no actinic or

Fig. 2.



photographic influence; though at F, near the point of greatest heat, D, the actinic or chemical influence is sensibly felt; this is ascribed by Claudet to the yellow rays being not merely passive or inert as regards actinic power, but having a positive destructive influence on any effects produced by the actinic rays.

Scheele was the first to show that the rays of the sun were able to effect chemical changes, more especially upon silver salts. He was followed by Senebier, Count Rumford, and Ritter, who was the first to notice that solar beams, not possessing luminosity, but having a remarkable effect in inducing chemical metamorphoses, existed in sunlight. Little was, however, done bearing upon the origin of photography, till Thomas, the youngest son of Josiah Wedgewood, in 1802 published his method of producing sun pictures, by coating white paper or enamelled leather with a solution of nitrate of silver, and exposing the coated surface to the light of the sun under a painting on glass. He did not succeed in fixing the impressions, though he was assisted in his research by Sir Humphrey Davy.

Nicéphore Niepce, born at Châlons-sur-Saone, was the first who succeeded in fixing the image in the *camera obscura;* and if we take photography to mean, not simply the superposing of an object upon a sensitive sheet and allowing the sun to print the outline of that object, but rather the reflecting of any image in nature in the camera, and fixing it after the image has passed away, then Niepce was certainly the first photographer.

It was as early as 1816 that Nicéphore Niepce first produced a veritable photograph in the camera; but in this instance the lights and shadows were inverted, that is to say, the whites in the original object were depicted in black in the picture, and *vice versa*. While these first experiments were being conducted by Nicéphore, his brother was in England endeavouring to sell a mechanical invention which the brothers had devised; and the letters which passed between them, and which have recently been published, explain very fully the nature of the early essays in photography. Nicéphore had heard of Senefelder's invention of lithography, and his idea was to reflect an image upon stone which should remain permanent after the shadow had disappeared. He contrived a *camera obscura*, fitted it with a lens, and forthwith began his research. His first photograph was obtained, as far as can be made out, by steeping white paper in salts of silver to render it capable of being blackened by daylight, and placing a sensitive sheet of this description at the back of the camera, where the reflected image could fall upon it. By these means he obtained landscape pictures, which, however, remained visible for a few weeks only, even when screened from the light. In his letters to his brother Nicéphore describes his progress very minutely—how he finds that sunlight is not absolutely necessary for the production of his pictures, but that diffused daylight would do; how, in order to obtain an image of sharper definition, he finds it necessary to contract the opening of the lens, and how he busied himself in endeavouring to transpose the lights and shadows. The following is a description of his method of placing his camera in position to begin work, extracted from a letter dated 5th May, 1816, to his brother:—"I placed my apparatus at the open window of the room where I operate, in front of the pigeon house, and made an experiment in the usual manner. I obtained on the white paper the whole of that portion of the pigeon house which is seen from the window, and a faint image of the casement, which was less brilliantly lighted than the exterior objects, the image reflected being of the most minute proportions." On the 19th May following, we have a description of the first photographs from nature that were ever taken in a camera:—"I have to enclose two pictures taken by my process. . . . . You will be able to judge of the effect better by placing yourself somewhat in the shade and holding up the pictures, placed upon an opaque body, against the light. A picture of this description is, I believe, subject to alteration after a time, as, although proof against the action of light, the reaction of the nitric acid in its composition will have the effect of destroying it. . . . . My future investigations will be conducted with a threefold object—(1) To obtain a clearer definition of the reflecting image; (2) to transpose the tints or shadows; (3) to fix the tints, an operation which is by no means an easy one." These extracts prove clearly that Nicéphore Niepce was on the right track to discover photography; and a further quotation from a letter, dated 28th May, 1816, gives quite a circumstantial account of his pictures:—"I send you herewith four new prints, two large and two small ones, which I have obtained of sharper definition by the adoption of a very simple plan, which consists in contracting, by means of a disc of cardboard, the diameter of the lens. The interior of the

camera being less illuminated, the image becomes sharper, and the outline, as likewise the lights and shadows, are much more clearly defined. You will be able to judge by the roof of the pigeon house, by the angles of the walls, and by the casement, in which the window frames are distinctly visible (in certain places the glass even appears perfectly transparent); and, lastly, you will see that the image retains the exact tints or colours of the original object. If the picture fails in definition, it is simply, on account of its minute size; and the original would be quite as ill-defined if viewed from a corresponding distance. . . . . The pigeon house is reversed in the pictures, the barn, or rather the roof of the barn, being to the left instead of to the right. The white mass which you perceive to the right of the pigeon house, and which appears somewhat confused, is the reflection upon the paper of the pear-tree, which is some distance further off; and the black spot near the summit is an opening between the branches of the trees. The shadow on the right indicates the roof of the bake-house, which appears somewhat lower than it ought to be, because the cameras were 5 feet from the floor. Finally, those little white lines marked above the roof of the barn are the reflection on the retina of the branches of some trees in the orchard. The effect would be much more striking if, as I told you, the lights and shadows could be inverted." After this NIEPCE endeavoured to obtain images of the same kind upon stone and metal; but it was not until 1823 that he succeeded in securing a really permanent photograph. This was done by means of an asphaltum, termed bitumen of Judea, which is soluble in certain oils in its normal condition, becoming insoluble after exposure to the action of light. By coating a metal plate with a solution of this material and exposing the same in a camera, an image was obtained which was rendered visible by afterwards washing the surface over with animal oil of Dippel, the latter substance being capable of dissolving away such portions of the bitumen as had not been fixed by light; the insoluble portion of the bitumen, remaining on the plate, formed the picture. Several specimens of these photographs are still extant in the British Museum and the Louvre.

It was not until after this date that DAGUERRE appears to have made photography his study. The two investigators were made known to one another by the circumstance of a relative of NIEPCE showing, in 1825, one of the bitumen pictures to CHEVALIER, of Paris, who then remarked that DAGUERRE had been making experiments with the camera also, but apparently with little success. In 1827 NIEPCE saw DAGUERRE in Paris for the first time, while on his way to visit his brother in England; and these relations ended two years later in a partnership to work out the invention between them. NIEPCE previously, however, came to England, as we have just stated, and brought with him some of his pictures, which he was desirous of submitting to the Royal Society; but as the method was maintained a secret, that body refused to listen to the inventor. NIEPCE then sent his process to the king, but with no greater success. He lived near Kew, and during his sojourn in this country secured a picture of Kew Church, which is still in the British Museum. He returned to France in January, 1828; and his attention was then called to an improved camera devised by DAGUERRE, and it was this incident that suggested the formation of a partnership between them in 1829.

DAGUERRE was a painter of some eminence, and director of the Diorama in Paris. For some time it was known he had been endeavouring to fix the image reflected in the camera; and although he asserted he had been successful in his attempt, no evidence of the fact was ever shown. NIEPCE and DAGUERRE were brought into communication with one another; but it should be borne well in mind that before the two investigators knew each other, NICÉPHORE NIEPCE had already become a successful photographer. The deed of partnership is still extant; and a fac-simile of it, printed by means of photo-lithography, is contained in a work entitled "La Verité sur l'Invention de la Photographie," by M. VICTOR FOUQUE. This document states that a partnership was entered into, under the title of NIEPCE-DAGUERRE, in order to elaborate a process *invented* by NIEPCE and *improved* by DAGUERRE—the former, as his contribution to the concern, agreeing to make known all details of his invention, and the latter contributing a new form of camera and the benefit of his study and labours. The contract was to last ten years, it being expressly stipulated that in case of the invention ever being published, it should be made known under the title of NIEPCE-DAGUERRE; and should either partner die before the expiration of the period agreed upon, the natural successor of the partner so dying should fill the vacancy. The contract contains a most interesting account of NIEPCE'S early experiments, and of the results he had obtained up to that moment. But although it includes full details of NIEPCE'S work, there is not one word of DAGUERRE'S results; and we must infer, therefore, that till that date nothing of a practical nature had been secured by the junior partner.

Two years after the drawing up of this compact NICÉPHORE NIEPCE died, and his place was filled up by his son ISIDORE. Meanwhile DAGUERRE worked away at the invention; and in 1839 he sent for ISIDORE, and informed him he had discovered a most practical and efficient method of photography, quite distinct, however, and unconnected in every way with the invention of the elder NIEPCE, and this DAGUERRE refused to publish except under his own name. ISIDORE protested for some time; but, like Esau, ultimately sold his birthright for a consideration. DAGUERRE thereupon made known the process to the Academy of France, omitting all mention of NIEPCE, and claiming for himself the whole credit of the invention; and it was not until some time afterwards, when Daguerreotype had become an established fact, that the friends of NIEPCE came forward to claim for the original

investigator a share of the honour. Foremost among these was Bauer, the secretary of the Royal Society, who on the publication of Daguerreotype called attention to the fact that Niepce had invented a similar process, and had shown in this country pictures obtained by its means more than ten years previously. Faraday added his testimony to the fact when he was shown examples of Daguerreotype, for he had himself seen Niepce's sun pictures many years previously. Daguerre asserted his invention to be totally distinct from that of Niepce, and in no way based upon it; while, on the other hand, the Niepce party contended that Daguerreotype was a modification of what ought to have been termed Niepçotype. In the end the French government awarded 4000 francs as annual pension to the son of Niepce, and 6000 francs to Daguerre.

If we for a moment compare Daguerreotype with Niepce's invention, we at once see the analogy between them. The former may be divided into four operations:—1, to clean the metal plate; 2, to render it sensitive; 3, to expose it in the camera; 4, to develop the image. Niepce's description of his process, as we have it in his own words, is as follows:—"I first take a metal plate—either of tin, copper, or silver, but I prefer the first—and this I coat with a film of bitumen of Judea, which is sensitive to light; I then expose the plate in the camera, and afterwards wash it in oil of almonds, to render the picture visible. I also use iodine, to render the image more black." Therefore, although Daguerreotype is incontestably a far superior process than ever that of Niepce was, it cannot be denied that some of the manipulations in both cases are the same, while the *modus operandi* is identical. Niepce mentions the use of a silver plate and of iodine, and actually hints at the employment of mercury—the three principal requirements in Daguerreotype; and besides this, the older experimenter made known the broad fact that a visible image is not at once obtained in the camera, but that it requires to be *developed* in a subsequent operation. To Niepce therefore belongs, rather than to any other, the honour of having discovered photography.

In England the subject was pursued by Henry Fox Talbot. His experiments were begun in 1834, with the view of rendering the image produced in the camera obscura on paper permanent in the sun, and were prosecuted with varied success till 1839, when a paper was read by him to the Royal Society on the 31st of January of that year, entitled, "Some Account of the Art of Photogenic Drawing; or, the Process by which Natural Objects may be made to delineate themselves without the aid of the Artist's Pencil." In February of the same year a fuller account of the preparation of the paper, and the method of fixing the picture, was communicated to the same body. This mode of photography was termed the "Talbotype process."

The fixing agent first used by Talbot was a concentrated solution of sodium chloride, which had the effect of dissolving the unaltered silver chloride. Potassium iodide was employed for a similar purpose. The use of hyposulphite of soda (chemically, sodium thiosulphate, $Na_2S_2O_3$) was proposed by Sir J. Herschel. Other improvements by the latter philosopher have also to be recorded, which, though less important than the one just referred to, contributed, nevertheless, to the perfection of the art.

Herschel was the first to saturate the saline washes used to prepare the paper with chloride of silver, and to wash with nitrate of silver twice successively, drying the paper between each dipping, and thus doing away with the whitish spots so frequently seen in the pictures of Talbot at the time. He also noticed, as likewise did Robert Hunt, a method of fixing the impression formed in the camera with chloride of mercury, nothing being required to develop the picture but simply washing with hyposulphite of soda.

Another very important discovery of Talbot's was, that treatment with gallic acid renders the prepared paper so sensible as to receive impressions by instantaneous exposure, owing to the gallic acid of the ingredients continuing and developing the effect of the sun's rays. This improvement led the way to the use of pyrogallic acid (by Archer), the reducing or developing action of which is much greater than that of the gallic compound.

Subsequent to the production of photographs on paper, glass was adopted for the basis of the picture; but as the sensitive media could not be made to adhere to this body alone, it was necessary to employ as an adjunct some adhesive matter. The first trials were with albumen and gelatin, laid in a thin stratum upon the clean surface of the glass, by Niepce St. Victor, in 1848. Potassium iodide or alkaline chlorides were mixed with the adhesive composition; and after partial drying, the surfaces were rendered sensitive by solution of silver nitrate. The pictures obtained on albumenized or gelatinized glass, owing to the even and close texture of the coating material, had many qualities superior to those produced upon paper. Soon after this time Archer substituted collodion for these media. With the exception of modifications introduced from time to time to render the collodion film more sensitive, or to extend the chemical action set up by the rays of light, and thus shorten the period of exposure, very little has been done within the last few years beyond rendering the art more general both in practice and application.

It has long been sought to perfect the photographic process by rendering the images capable of being printed from. These attempts are not recent, but as old as the first bituminous impressions of M. Niepce, whose finished pictures required but the application of the etching liquid to convert them into engravings. This system has been worked out by Niepce the younger, Lerebours, and Lemercier, the latter applying it to lithographic printing. Dr. Dorme of Paris partially succeeded in obtaining engravings from daguerrotype plates. His method was to attack the plates with nitric acid before the gilding of the picture, when all the parts whereon

the silver was reduced became more or less corroded according to the depth of shade. Sir William Robert Grove published a method for engraving the daguerrean image by voltaic agency in 1842: the active agent was chlorine liberated from hydrochloric acid, in which the picture, attached to the positive pole of the battery, was immersed. A patent was granted in 1844 to Fizeau and Claudet for engraving photographic impressions. Here hydrochloric acid, liberated from a mixture of sodium chloride and potassium nitrate, to which a little nitric acid had been added, was the etching medium, and ammonia and a hot concentrated solution of caustic potash the auxiliaries to it in bringing the process to perfection; the former having the effect of removing the chloride of silver, and the latter protecting the surface coated with the mercury from the corroding action of the acid. When sufficiently deepened the plate was washed and dried, smeared with printers' ink, dried, cleaned, and the unetched parts gilded, after which the remaining parts could be deepened at will by first removing the ink. H. F. Talbot's method, published in May, 1853, seemed to be satisfactory. It consisted in coating a well-polished steel plate with a mixed gelatin impregnated with a strong solution of potassium bichromate; and when dried, exposing this plate to the sun's rays, with a positive photographic picture superposed. As in the case of Niepce's bituminous method, the influence of the light rendered the parts on which it fell insoluble, so that on subsequent washing in water the gelatin and bichromate solution were removed from the other parts, leaving a raised facsimile of the picture, the lights being represented by the bare metal, and the shades, corresponding to the lights in the original, by the altered gelatin. On pouring platinum bichloride upon the washed surface, the plate is readily etched on the parts from which the gelatin was removed. When the action has been sufficiently continued, it is arrested, removing the gelatin with a sponge, and drying. The plate now exhibits a delicate etching of the picture on the steel plate, in which the raised surface corresponds to the light and half tones of the original design. Pretsch of Vienna published a method for effecting the same purpose; it has much in common with Talbot's, but instead of washing off the coating of gelatin, as directed by the latter, it is merely soaked in water, to swell the unaltered gelatin, and give the appearance of an engraved wood-block to the figure. An impression of the figure is then taken with a soft material in the way of a mould, and the latter is rendered a conductor of electricity, and copper is deposited upon it to any desired extent. In this way a true impression is taken of the photograph in copper, and may be multiplied at pleasure. Lastly, Duncan C. Dallas has worked out a good engraving method from metal plates, which he terms photo-electric engravings.

Efforts have been made to impress the tints of the object upon the picture by chemical agency, and sufficient indications have been given to show that the subject is feasible of attainment. In chromo-photography, or heliochromy, as the process was called in France, Becquerel, in 1854 and previously, showed that colours could be impressed on the picture at the instant of its formation, by employing the violet chloride of silver—a compound in which more or less of a basic chloride exists—for taking the picture. To give the subject more definition, he coated the silver plates by means of chlorine liberated from hydrochloric acid by voltaic agency, and in which solution the tablet was immersed, attached to the positive pole of the battery. As it was found that the shades were much altered by the thickness of the coating of the violet chloride on the plate, he introduced a voltameter of water in the circuit, to measure from the volume of hydrogen disengaged the quantity of chlorine set free; and by this means he was able to determine the quantity of gas that passed over a given extent of the plate. When a plate so prepared was exposed in the camera to the solar light of the spectrum, all the chief colours were produced, beginning with the yellow and orange, and extending to the red and violet, thus leaving a coloured picture. As these hues could not be fixed so as to resist the effect of diffuse light, they were looked upon more as a scientific curiosity. Niepce St. Victor, being led to infer a relationship between the colour which many bodies communicate to flame and that which light developes in a plate of silver coated as above, tried the effects of silver plates excited in chlorine water impregnated with various salts, such as chloride of strontium and the like, and placed the plate in the camera for the reception of the rays from coloured bodies, when the image became impressed with the natural tints of the subject. Thus, an orange was obtained by the use of calcium chloride, yellow by sodium chloride or chlorine, red with strontium chloride, green with boracic acid and nickel chloride, and so on, employing for any particular shade a substance which similarly colours the blowpipe flame.

The chromo-photographs of Niepce St. Victor, consisting for the most part of dolls dressed in coloured raiment, are still in a good state of preservation, although eight or ten years have elapsed since they were taken; not being proof against daylight, they are kept in closed boxes, and may only be viewed by candle light or other subdued illumination, but they are still very creditable productions.

Poitevin in France has also reproduced natural colours on violet subchloride of silver applied to paper; and Wharton Simpson in this country has also secured natural colours impressed upon subchloride of silver in a collodion film.

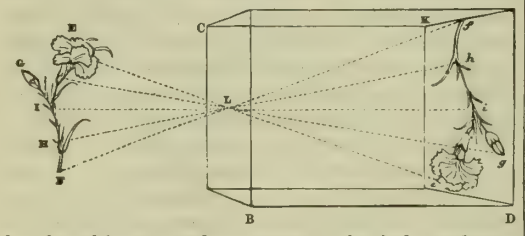
The art of photography is dependent partly on optics, and partly on chemistry. It is the business of the optician to provide a suitable camera in which the photographic tablet may be placed, and the image formed by the lens thrown upon it.

The simplest form of camera obscura is a dark box, having a small orifice in the centre of one end, and a focusing screen of ground glass at the other. On throwing a black cloth over the head and camera, and looking at the focusing screen, an inverted image

is seen of the object towards which the opening of the camera is presented. When the hole is large, this image is bright but indistinct; by reducing its size, the image becomes more distinct, but fainter. The brightness and size of the pictured objects depend upon the distance of the focusing screen from the hole; and the smaller that distance may be, the smaller are the objects and the brighter the picture. The shape of the aperture does not determine that of the picture or the outline of the objects, a triangular hole giving the same image as a round one. The image formed in this simple camera, although more or less indistinct, is absolutely free from distortion, and the rules of plane perspective are strictly fulfilled.

To understand the principles on which the cameras are constructed, it must be remembered that every visible object of which an image can be formed by a lens, is supposed in optics to consist of an assemblage of luminous points, from each of which rays of light proceed in all directions, but without interfering with each other; and an assemblage of rays proceeding from any single point is called a *pencil*. A bright object, therefore, emits a pencil of light from each of the bright points composing it. Let E F, Fig. 3,

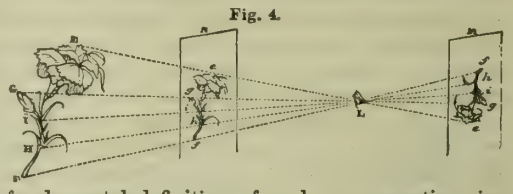
Fig. 3.



be the object, B C the camera, L the hole, and K D the focusing screen; then a pencil of light proceeding from E passes through the hole L, and the rays continue onwards until they reach the focusing screen at *e*, at which point a spot of light is produced of the same shape as the hole at L, but somewhat larger than it, and of the same colour as the point E of the object. Similarly the points F, G, H, I, &c., emit pencils which after passing through the hole illumine the spots at *f*, *g*, *h*, *i*, &c., and in this way an indistinct inverted image of the object is formed. The size and shape of the image do not depend upon the opening, because the luminous points of the object being infinite in number, and in close juxtaposition, the spots of light which compose the image, although individually of the same shape as the holes, glide one into the other, and form a continuous outline, in which all trace of the form of any particular spot is destroyed.

To show that the image upon the focusing screen is a correct perspective view of the object, the following illustration is submitted:—Suppose that L, Fig. 4, is the eye of a spectator, which is considered to be a mathematical point, and that straight lines, called *visual rays*, are drawn from L to the several points of the object E F; these straight lines constitute the edges of a system of pyramids, of which L is the common vertex, and if these are cut by any vertical plane at N between L and the object, the section is a plane perspective view. This is the

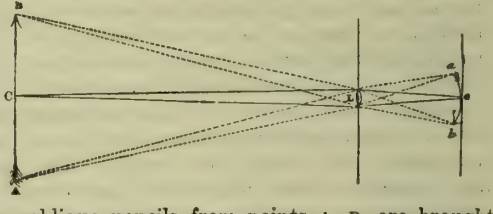
Fig. 4.



fundamental definition of a plane perspective view. Now, let it be supposed that the visual are rays produced through L, so as to form another system of pyramids on the opposite side of it; it is evident that if this second system be cut by a plane at M parallel to that at N, and at an equal distance from L, the inverted image thus formed would be an exactly equal and similar geometrical figure to the image at N, and the two figures would coincide if one were laid against the other. But the image at M is that which would be formed by a camera having a hole at L, and a focusing screen at M; so that this simple camera gives a correct perspective view of the object as seen from the aperture, and depicted upon a plane surface as far in front of the hole as the focusing screen behind it.

The simplest form of lenticular camera is that in which a very small convex lens is placed at L, Fig. 5. A direct pencil diverging from a point, C, of an object is then, after refraction through the lens, brought to a focus at *c*, where a distinct image is formed; but

Fig. 5.

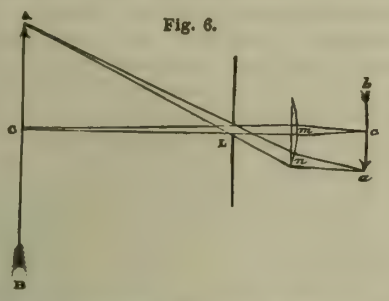


the oblique pencils from points A, B, are brought approximately to foci at points *a*, *b*, upon a circular arc, of which L is the centre, and L *c* the radius, and the rays, after passing through the points, *a*, *b*, again diverge and produce round spots or discs of light upon the screen, instead of a sharp focus as at *c*; the true image of the object being curved, as shown in the figure. A small single lens, therefore, gives so much curvature of the image as to render its margin very indistinct compared with the centre. It will be observed, however, that the image formed by a small single lens is free from distortion, because the axes of the pencils do not suffer deviation by passing through it.

In order to increase the radius of curvature of the image, the following plan has been adopted in the lenses used by photographers for taking views. Instead of placing a small lens at L, a large one is fixed at some distance behind L, as in Fig. 6. A central pencil from C is refracted through the centre, *m*, of this lens, and an oblique one from A, after

passing through the hole at L, is refracted near its circumference at *n*. This renders the image much flatter; because the distance, *n a*, which is equal to

Fig. 6.



the focal length, *m c*, of the lens, is measured from *n* and not from *m*, as in the case of a single lens placed at L. But this arrangement is open to the very serious objection, that the image is greatly distorted, in consequence of the axes of the oblique pencils being bent out of their course by refraction through the circumference of the lens, which acts as a prism in causing rays to deviate *from* its edges, and therefore the marginal parts of the image are too small for the central; besides, all straight lines in the image which do not pass through the centre are curved inwards at their extremities; so that in this form of view-lens flatness of field is gained at the sacrifice of true perspective.

The form of this lens is meniscus, or concavo-convex, the concave side being turned towards the objects; and the radius of curvature of the image is equal to the focal length of the lens, plus the radius of its convex surface; it is, therefore, longer by the latter quantity than the radius of curvature of the image formed by a small single lens without a diaphragm in front.

All photographic lenses require to be achromatized, or so constructed as to refract the different colours equally, in such a way that the yellow and violet foci may coincide; because the yellow rays produce the *visible image*, while all the rays of the spectrum which lie between the green and the extreme lavender produce more or less chemical effect upon the sensitive photographic tablet. The common view-lens is an achromatic meniscus, and may be achromatized in two different ways, one of which consists in placing a double concave lens of flint-glass before

Fig. 7.

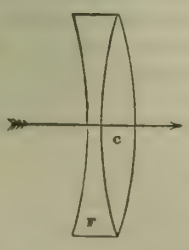
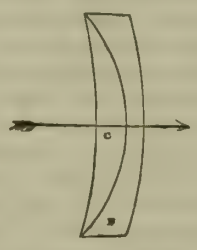


Fig. 8.

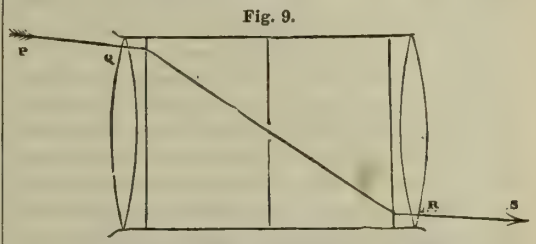


and in contact with a double convex lens of crown-glass, as shown in Fig. 7; and the other, in placing a concavo-convex lens of crown-glass before and in contact with a concavo-convex lens of flint-glass, as shown in Fig. 8. The effect of these combinations arises from the circumstance that flint-glass and crown-glass possess very different powers of *dispersing* or of separating the rays of light.

In the preceding figures, C denotes crown, F flint-glass. Both forms have equal radii of the front and back surfaces, equal focal lengths, equal curvature of the image, and an equal distortion; but the plan shown in Fig. 8 is the best, because there is rather less spherical aberration.

The best form of *view-lens* for giving pictures entirely free from distortion is a combination of two achromatic plano-convex lenses, with the convex sides outwards, and a small stop midway between them, as shown in Fig. 9. If a ray, P Q, be

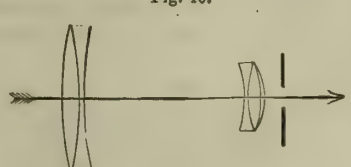
Fig. 9.



refracted through this combination in such a way that its course between the lenses passes through the centre of the stop, it is evident, from the symmetry of the figure, that the emergent ray, R S, will be parallel to P Q; from which it follows that the axes of pencils refracted through this combination do not suffer deviation, and therefore there is no distortion in the image. The curvature of the image is, however, greater than with the single view-lens, and the central definition, when the diaphragm is removed, not quite so good as that of the *portrait-lens* to be described presently.

The best view-lens for combining tolerable freedom from distortion, with flatness of field and perfection of focus—that is to say, the most generally useful view-lens—is that of Professor Petzval of Vienna, and commonly called the *orthoscopic lens*, from the fact that the straight lines of objects are not curved in the image. Its construction is shown in Fig. 10. The front lens is achromatic and con-

Fig. 10.



vexo-concave; and the back lens achromatic, and composed of two, which only touch at the edges. The inner one—that is, the one next to the front lens—is of crown-glass and double concave, with the deepest concavity next to the meniscus; the outer one is a meniscus of flint-glass. The front lens of the combination is convex, and brings rays to a focus; the back lens is concave, and scatters

them. In order to improve the definition, and bring objects at different distances into good focus, a stop is placed immediately behind the back lens. The distance between the front and back lenses of the combination is about equal to half the diameter of the front lens, and the diameter of the back lens is about two-thirds that of the front one. In this combination the oblique pencils pass near the circumference of the front, and through the centre of the back lens; they are therefore lengthened, and the consequence is the production of a very flat field. A small amount of distortion is produced by this instrument, which causes straight lines not passing through the centre of the picture to be curved *outwards* at their extremities, and the objects at the margin of the field are rendered proportionally larger than those in the centre; but these defects exist to a much smaller extent than those of an opposite kind in the single view-lens.

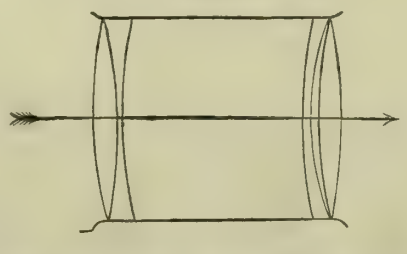
There are, therefore, three different view-lenses used by photographers, namely—the single view-lens, with a stop in front, which gives a flat field, but great distortion; the symmetrical double combination, which gives an image entirely free from distortion, but having considerable curvature; and the orthoscopic combination of Petzval, which gives a tolerably flat field, and the image *nearly* free from distortion. The second lens is the best when a sufficiently small stop can be used to obtain good marginal definition. In other cases the orthoscopic lens is the best, and the single view-lens the worst.

The view-lens includes an angle of from 35° to 40°. It cannot be used for portraits in a glass room, because it would require too long an exposure.

The *portrait-lens* commonly used is that which was invented by Professor Petzval about seventeen years ago. In this combination everything is sacrificed to getting a large central pencil free from spherical and chromatic aberration. The curvature of the image is considerable, and the angular field of view rarely exceeds 20°. Its merit is quickness of action, which is absolutely required in photographic portraiture. As soon, however, as more rapid processes are discovered, the portrait-lens, with its large aperture and many unavoidable defects, may be given up.

The construction of the portrait combination of Petzval is shown in Fig. 11. The front lens is

Fig. 11.



achromatic and convexo-concave, the lenses being in contact. The back lens is achromatic, and formed of two lenses separated by a small interval; the inner one is of flint-glass, and convexo-concave, the outer one of crown-glass, and double convex, with the flatter side outwards. The focal lengths of the two compound lenses are nearly equal, the front lens having the longer focus, and both are convex lenses. The combined focal length of the instrument, measured from the back one, is from three to four times the diameter of the front lens.

Of late years very considerable improvement has been made in the construction of photographic lenses, and no one has paid more attention to the the subject than J. H. Dallmeyer, F.R.A.S., whose instruments, especially for portraiture, are more widely used both in this country and abroad than those of any other optician. For this reason we have deemed it expedient to quote the advice he gives relative to the choice and use of lenses; for this is a subject on which the photographer is, as a rule, lamentably ignorant. In regard to portrait lenses, says the author, they "are either more or less rapid in action as their diameters are larger or smaller, or as their focal lengths are shorter or longer. The focal length of a lens regulates the *size* of the picture, and the diameter expresses its *speed* or rapidity of action. Having fixed upon the size of the picture to be taken, the next thing to be determined is the most suitable focal length of the lens. This, however, involves the prior determination of the *distance* at which to place the subject; for, as every photographer knows, the placing of the lens nearer to the subject increases the size of the picture, and *vice versâ*. The question then arises, What is the proper distance at which to place the subject from the lens? In answer it may safely be asserted, that it should, as a rule, be not less than 12 feet, nor, perhaps, more than 24 feet. For if less than this, the resulting picture will generally be defective both in definition and perspective, because the lens producing it will be of too short a focus; and if the distance is greater, the resulting picture will probably be deficient in relief or roundness. This, because the atmosphere in our towns is seldom quite clear from fog or haze; and the greater the distance between the lens and subject, the more obviously will this haze be reproduced in the picture.

"A medium distance, therefore, of from 16 to 20 feet, should be chosen. For a distance, then, from 16 to 20 feet between the lens and subject, the equivalent focal length (not the back focus) of the lens for a given sized plate, should be about *twice* that of the largest size; that is, for a $4\frac{1}{4} \times 3\frac{1}{4}$ plate (*carte de visite* size), the focal length should be $4\frac{1}{4} \times 2$, or equal to $8\frac{1}{2}$ inches; for a 6×5 plate (cabinet size), 6×2, or equal to 12 inches; for a 10×8 plate, 10×2, equal to 20 inches, and so on."

Dallmeyer then proceeds to say that, having determined the *focal length* of the lens for a *given sized plate*, the next thing requiring consideration is its diameter, or rapidity of action. As a matter of course every photographer wishes to possess a quick acting lens; and not only this, but flatness of field and great "depth" of focus, or definition, as well:

forgetting all the while that these qualities are almost diametrically opposed to one another. Thus of two lenses of the same focal length, and both perfectly corrected for spherical aberration, the one of 2 inches will have twice the depth of another of 4 inches in diameter; whilst the latter, in turn, is four times quicker in action than the former.

As regards the use of portrait lenses, the following is well to the point; for it gives, in a few words, just those particulars relating to adjustment of camera, &c., which are valuable in practice:—

"For a card portrait, distance of subject 18 feet, the camera being without a swing back, arrange as follows:—Height of centre of lens from the floor, about 4 feet 10 inches; rising front of camera elevated a quarter of an inch; let the image occupy the centre of the plate—*i.e.*, the head and feet equidistant from bottom and top of screen. To effect this, the camera requires tilting forward slightly. Tilting the camera forward is an advantage, for it produces a more natural view of the face, and is preferable to its being placed lower and level, which latter position implies a looking *up* into the face, and produces neither a natural nor pleasing picture. The image occupying the centre of the plate, proceed to focus for the eye, and then for the chest, or for some prominent object on the chest, as a watch chain, for instance; now halve, as it were, the focus between this and the eye, when it will be found that the resulting picture will be evenly defined throughout its entire length."

Again—"In placing the accessories of a portrait, or in disposing the positions of a group of persons, regard should always be had to accommodate as much as possible the curvature of field produced by the lens; and this is accomplished by arranging the group or accessories in approximation to a curve—that is, objects at the sides should be brought nearer to the lens than those occupying the centre; the image then falls on a *plane*, and this is what is required. The amount of curvature of field varies in different lenses, and hence definite rules for placing the objects composing a picture to suit this curvature cannot be given, but one or two trials will at once determine this question."

As regards landscape lenses, says Dallmeyer, all the most eminent landscape photographers are unanimous in recommending the "single combination" for simple landscape work; for the obvious reason that this lens having but two reflecting surfaces, the rest being cemented, produces the most brilliant pictures; and on account of its form, it has more depth of focus than a "double combination" lens. Moreover, the former produces an evenly-defined image with a comparatively large stop, and hence it is more rapid in its action. The drawback to the "single combination" is the distortion it imparts to any architecture on one side of a picture, but this may be obviated by taking care that no buildings are depicted at the margin of the plate. Among view lenses of this kind, the *smaller* the diameter, it should be borne in mind, the better the lens. For architectural purposes a lens giving straight lines is indispensable, and a rectilinear lens must therefore be employed; a careful adjustment of the camera is likewise invariably necessary. In regard to landscape work, Dallmeyer gives most excellent advice, which every photographer should take to heart.

"In the selection of a view always aim as much as possible to favour the natural curvature of field as produced by the lens—*i.e.*, if possible let the side objects be nearest to, and the centre ones farthest away from, the camera. When photographing a flat object (as a block of buildings), or when copying a map or plan, focus for a point one-third from the centre, and the resulting picture will be approximately equal in definition throughout.

"Always work with the largest possible aperture or stop if you wish to secure relief and atmosphere in your picture. Proceed as follows:—Focus for the object—*i.e.*, that which is to constitute the point of *interest* in the picture, and which is generally near in the foreground. Do this with a medium stop. When done, look to the distance and other objects in the picture, and only reduce the aperture just so much as will prevent these appearing foggy. But do not aim at equal sharpness everywhere if you wish to produce a *picture*, for what artist would think of painting his background or accessories as sharp in outline as the *subject* of his picture? And who ever saw the distance perfectly sharp in nature when the eye is adjusted upon some object near in the foreground? Photography is claiming higher ground than the old standard of excellence—viz., *sharpness* everywhere—and those who aim at *artistic photography* may find the above hints of some service."

Practice of Photography.—In the images formed in the camera obscura the lights and shades are true to nature, but the position of objects is reversed, as regards right and left. In fixing these images by photography upon various tablets, the object is to produce impressions true to nature in the lights and shades, and non-reversed.

There are two ways of doing this. According to one method a *negative* photograph is first produced, from which, by a second photographic process, a *positive* photograph is obtained. The other method consists in obtaining a positive photograph by one operation.

By a *negative* is meant a transparent photograph in which the lights and shades are the opposite to those in nature, and the objects reversed as regards right and left. By a *positive* is meant a photograph in which the lights and shades are true to nature.

Two direct positive processes are commonly used; they are called the *daguerreotype* and the *positive collodion* processes. In the former the picture is produced upon a silvered copper plate; in the latter upon glass, or some smooth black substance, such as glazed leather, oil-cloth, enamelled iron, &c.

The Daguerreotype Process.—This process is now hardly ever practised in Great Britain, and but partially in America; nevertheless, a short description of it is necessary:—A silvered copper plate is

first polished to the utmost; it is then rendered sensitive to light by being exposed to the fumes of iodine and bromine, after which it is presented to the image in the camera. No visible picture is produced until the plate is submitted to the vapour of mercury, which adheres only to the parts that have been acted on by light, thus forming the lights of the picture, whilst the blackened polished metal forms the shadows. The subsequent operations consist, first, in removing the film of silver iodide and bromide from the plate by immersing it in a solution of hyposulphite of soda (sodium thiosulphate), and next in fixing the picture permanently to the plate by means of a boiling solution of "sel d'or"—hyposulphite of gold and soda, which at the same time greatly improves the appearance of the picture. Such is a brief sketch of this very beautiful process. It now remains to describe the operations more in detail.

To Polish the Plate.—The plates are polished by dusting a little finely-powdered rotten-stone upon them, and rubbing them all over with a little cotton or fine flannel dipped in a solution of nitric acid in 20 parts of water. When all dirt is removed, they are dried by friction with fine dry cotton or flannel. Finally, the slight scratches produced in the first operation are effaced by rubbing the plates on pads of velveteen nailed to a board, and upon which powdered charcoal of different degrees of fineness is laid. When perfectly clean and polished, the breath will condense upon it in an even sheet.

To Excite the Plate.—Two coating boxes are required for this operation, one containing iodine, the other lime saturated with bromine. The iodine is spread evenly over the bottom of one of these boxes, and the bromide of lime to the depth of an inch over the bottom of the other. The plate is then laid face downwards over the iodine, for a minute or two, until it assumes a deep yellow colour; it is then removed, and laid over the bromine until it assumes a bluish steel colour; and then again over the iodine for a few seconds, after which it is ready to be exposed in the camera. In exposing the plates to the exciting media the time of exposure is dependent on the temperature of the room, and consequently there is nothing to direct the operator, except the tint of colour on the polished surface mentioned above. The plate may be examined under a feeble light until it is put over the iodine the second time; and should any accident occur in taking a picture, and the plate be exposed to light, there is no necessity to clean and excite it again; for the mere exposure to iodine for two or three seconds will obliterate the impression, and render the plate in as good condition for receiving a fresh impression as it was before.

The Exposure in the Camera.—The exposure in the camera and development of the image should follow the exciting of the plate as quickly as possible; nevertheless, if the sensitive plates be put into a closely-covered plate box, face to face, they preserve their sensitiveness for some hours unimpaired.

The time of exposure in the camera can only be ascertained to great nicety by experiment. The process is exceedingly sensitive and rapid, and with the full aperture of a portrait-lens, and a strong light out of doors, an instantaneous exposure is sufficient; but under glass, and with a moderate diffused light, several seconds are required, and with a view-lens and small diaphragm several minutes; everything depends on the brightness of the object and the size of the diaphragm.

The over-exposed parts of a picture look blue; the under-exposed parts black and devoid of detail. The photographer should avoid as much as possible too violent contrasts of light and shade in the model, and aim at half tone and modulation of shade; and in exposing a plate, the exposure should be timed with reference to the shadows, and the lights left to take care of themselves.

The Development of the Image.—On removing the plate from the camera, it is placed in a mercury box containing the vapour of mercury heated to about 140° Fahr. (60° C.). The most convenient mercury box is made of iron, and shaped like an inverted pyramid, the mercury being at the bottom, and the plate laid horizontally over it. It is provided with a thermometer which indicates the temperature, and the mercury is heated by a spirit-lamp placed underneath. The surface of the mercury should be perfectly clean; this is secured by frequent filtering, either by squeezing through a wash-leather, or passing through a glass filter with a small aperture made for the purpose. The time of development depends upon the size of the box, the temperature, and the quantity of quicksilver used, and may vary from two to three minutes to a quarter of an hour—about five minutes is a good average time. The development should not be stopped until all the details in the shadows are fully out. If continued too long, or if the mercury be too hot, the picture appears hazy, the shadows assuming a peculiar speckled appearance.

The Fixing and Gilding.—On removal from the mercury box, the picture may be exposed to daylight, as no further change can take place. In order to remove the iodine and bromine from the plate it must be immersed in a solution of hyposulphite of soda in distilled water. The strength is immaterial, 1 part hyposulphite to 6 parts of water answers well, but it is important always to filter the solution. It should be poured into a flat dish, and the plate immersed face upwards in such a way as that a wave of liquid flows quickly over it, and two waves not allowed to meet upon it in any part. The yellow film upon the plate is thus quickly cleared off, and the polished silver with the grey image upon it exposed to view. The plate must then be well washed with distilled water, drained, and laid accurately horizontal upon a levelling stand, ready for the operation of gilding. This is accomplished by pouring upon the plate through a funuel, having a tuft of cotton wool in its neck, as much of a solution of hyposulphite of gold and soda—"sel d'or"—as it will hold without any running over, and then heating to the boiling point by passing a spirit-lamp backwards and forwards under the plate. The sel d'or solution is made by dissolving half a grain of the

compound hyposulphite in 1 oz. of distilled water. While boiling the solution upon the plate bubbles form, but must not be allowed to stick to it; this is prevented by tapping the foot of the levelling stand occasionally with the bottom of the spirit-lamp, and thus communicating a vibration to the plate. As soon as the liquid becomes hot, the lights of the picture darken; but after a few seconds they begin to get whiter, and the blacks blacker. In the course of a minute or two the appearance of the picture is greatly improved, and the process is then arrested by pouring off the hot liquid, and washing the plate with cold distilled water poured over it from a bottle having a glass tube fitted into the cork; after which it only remains to dry the plate, and the picture is finished. This is done by taking the corner of it in a pair of pincers, holding it at an angle of about 45° to the floor, and passing the flame of a spirit-lamp underneath, beginning with the upper corner, chasing the line of wet from the upper to the lower corner, and removing the last drop with blotting paper.

The rationale of the daguerreotype is readily understood. A film of iodide and bromide of silver, sensitive to light, results from the exposures in the exciting boxes. This attenuated coating is reduced by the chemical rays of the light impinged upon it to the state of a subsalt; and upon exposure to the mercurial vapour the metal deposits upon the part so attacked. All the unaffected argentine surface is deprived of the sensitive iodo-bromide of silver by the solution of alkaline hyposulphite; and the final treatment with gold solution has the effect of depositing the gold by electrolysis upon the parts of the plate acted upon by the light.

The daguerreotype process stands unequalled for microscopic perfection of detail, modulation of shade, and beauty of half-tone.

Daguerreotypes are permanent when the manipulation is properly performed, the plate thoroughly washed, and carefully sealed up in an air-tight case. In order to avoid the reversion of the image a reflector must be used in front of the lens, an expedient which is not necessary in any other process.

The Collodion Processes, Positive and Negative.—Collodion, so named from its adhesive nature, is a gelatinous substance made by dissolving pyroxylin (gun-cotton) in a mixture of ether and alcohol. It is extensively used in photography as a vehicle for supporting the sensitive chemicals.

To make gun-cotton (which see *ante*) mix together in a large and perfectly dry basin equal parts, by measure, of commercial oil of vitriol and nitric acid, specific gravity 1·42. The temperature of the mixed acids rises to about 150° Fahr. (65°·5 C.), and must be maintained at that temperature by placing the basin in hot water. The operation should be conducted under a chimney in order that the fumes may escape. Then immerse in the mixture, in small quantities at a time, the best cotton wool, pulled out into thin flat pieces. Put as much into the liquid as it will conveniently cover, and stir it about with two thick glass rods for the space of five minutes. Then pour the whole contents of the basin into an earthenware colander, so that the acids may drain off, and wash the cotton thoroughly by putting it for a minute under a tap; after which throw it into a pail of water, and stir it about with the glass rods. Change the water, and continue this washing for some minutes, squeezing the gun-cotton between the hands occasionally; and, lastly, put it into warm water, to which a little soda has been added, in order to neutralize completely all trace acidity; after which wash the gun-cotton again of thoroughly in several changes of water, and let it soak in water for an hour or two; then remove it, squeeze it, and spread it out to dry, or hang it up in a net suspended from the ceiling. When nearly dry pull it out into small pieces or tufts, and in this state let it get thoroughly dry. It should then be put away in a tin canister. It is an exceedingly inflammable and dangerous substance, and has been known to decompose by keeping, and evolve dense suffocating fumes. Great care should therefore be taken in its manufacture and preservation.

The proper strength of the nitric acid should be strictly observed; for there are several kinds of gun-cotton, some of which are quite unsuitable for the purpose. For instance, if the strongest nitric acid is used, specific gravity 1·5, the gun-cotton is of the most explosive kind, and will not dissolve in ether and alcohol; if, on the other hand, the nitric acid be too weak, the gun-cotton is but imperfectly soluble, and a good deal of it becomes disintegrated, and is lost in the washing. But even supposing the gun-cotton to dissolve perfectly in the ether and alcohol, the collodion may still be faulty; for if the acids are too strong, the collodion film when spread upon a glass plate contracts greatly on drying, and if too weak, the film is opalescent, and partially opaque like tissue paper, instead of being transparent and structureless. Then, again, if the temperature of the acid mixture be too low, the negatives are deficient in density; and if too high, the collodion becomes insensitive, and fails to give the half-tones of the picture; the blacks assuming excessive density, while the lights remain clear and devoid of detail.

"Plain collodion" is produced as follows:—Mix together absolute ether, specific gravity ·725, 1 part by measure, and absolute alcohol, specific gravity ·800, 3 parts by measure; and to every fluid ounce of this mixture add from 6 to 8 grains of pyroxylin, according to the thickness of film required. Shake the mixture well for some minutes. The pyroxylin quickly dissolves. The bottle should then be put aside, and remain undisturbed for several days, at the end of which time the clear liquid may be drawn off by means of a siphon from any sediment which may form, and it is then ready for use. The ether and alcohol employed may be either pure or methylated. Absolute methylic ether and alcohol answer the purpose exceedingly well, and are cheaper than pure spirits. They have also the advantage, that the iodized collodion does not become so quickly deteriorated as when pure spirits are used.

For making collodion, the following proportions by weight have also been severally recommended:—

Gun-cotton,	1	....	5	....	1
Ether,	120	....	110	....	196
Alcohol,	60	....	20	....	12

If the solution is too thick, it can be easily diluted to the suitable degree. This is known by pouring a small portion of it on a plate of glass, on which it should flow freely, and leave at the same time a firm film of collodion, and so cohesive as not to break under the stream of water. Any fibres of the cotton that may remain undissolved may be separated by filtration.

To iodize the collodion many receipts are followed. Archer's method is to make a saturated solution of potassium iodide in alcohol, and to add as much silver iodide as the liquid will dissolve, with repeated shakings; and after the menstruum clarifies, to add a sufficient quantity to enable it to take up a coating of silver from the argentiferous bath. Generally the iodizing solution is made differently for positives and negatives. For negatives it is made by dissolving 14 grains of potassium iodide to the ounce of alcohol, specific gravity ·825; for positives by dissolving 10 grains of potassium iodide and 2 grains of potassium bromide to the ounce of alcohol, specific gravity ·825. In order to iodize the collodion, 1 part by measure of the iodizing solution is added to 3 parts by measure of the plain collodion. The mixture is shaken well together, and may be used at once.

Monckhoven, in his treatise on photography, instructs the operator to bear in mind that if his normal collodion is too thin, it must be iodized with cadmium salt, which will make the solution thicker; while if the collodion is too thick, ammonium salt should be employed, which renders it thinner; potassium salts have no influence in this direction, and should therefore be employed when the operator is satisfied with the consistence of his normal collodion. Monckhoven's formula for normal collodion is—

Ether,	1 litre.
Alcohol,	½ "
Pyroxylin,	20 grams.

The liquid is allowed to stand for fifteen to twenty days, and is then decanted. It is iodized by mixing with an iodizing solution made up of—

Alcohol,	1 litre.
Iodide of cadmium or potassium,	40 grams.
Bromide of cadmium,	16 "

To every 75 parts of normal collodion are mixed 25 parts of the iodizing solution. The mixed collodion is almost immediately ready for use; it becomes tinted in a day or two, but is none the worse for such a change.

There are so many excellent collodions manufactured—Manson's, Blanchard's, Thomas', Rouch's, &c.—that photographers will find it much better to purchase the same ready prepared.

The Negative Collodion Process.—The operations for taking negative collodion pictures consist in cleaning the glass plate, coating it with iodized collodion, rendering it sensitive by immersion in the nitrate of silver bath, exposing it in the camera, developing the latent image, removing the redundant chemicals, and washing, drying, and varnishing the picture.

To Clean the Glass Plates.—Wash them well with water, and scrub them with a hard brush till they appear to be clean. Then rub them all over with a tuft of tow dipped in dilute nitric acid; wash them again thoroughly in several changes of water, or under a tap, wipe them dry with clean linen cloths, and finally polish them with a wash-leather or piece of cambric. When a plate is perfectly clean, the breath condenses upon it in an even sheet free from irregular markings.

To Apply the Collodion.—Hold the plate horizontally by one corner in the left hand, or put it upon a plateholder, blow off any dust that may have settled upon it, and pour in the centre of it a circular patch of collodion rather more than half as large as the plate. Then tilt the plate so as to allow the collodion to run towards the thumb, but without actually touching it, and afterwards to the adjacent corners, and pour off the surplus from the corner diagonally opposite to that by which the plate is held, into the bottle. After which rock the plate backwards and forwards with the corner upon the neck of the bottle, so as to prevent the formation of lines in the collodion; and place it upon the dipper of a nitrate bath, where it may remain from one to five minutes, according to the temperature. It is now ready to be excited.

To Excite the Collodion Film.—This is done by immersing the plate, as soon as the film has set, in a bath of nitrate of silver, made by dissolving 30 grains of pure nitrate of silver to the ounce of distilled water. The bath should be an upright vessel of glass or porcelain, and moulded in one piece. Gutta-percha is frequently employed; but although very good for the purpose, it is hardly so trustworthy as glass; and some operators have complained of gutta-percha baths communicating impurities to the nitrate bath, and putting it out of order. The plate should be completely immersed without pausing, as that would occasion a line across it. It should remain in the bath during a minute, moved up and down two or three times to take the ether from its surface, and allow an even coating of the silver salt to be formed. After this it is permitted to remain during two or three minutes longer, according to the temperature and the strength of the bath. Three minutes suffice when the bath is at 60° to 65° Fahr. (16°·5 to 18°·3 C.). The film will now exhibit an even coating of yellow iodide of silver. It should be drained for a few seconds over the bath, the back of it wiped with blotting paper, and then put into the dark slide.

It is important that the nitrate bath be made with pure nitrate of silver. When common commercial nitrate of silver is used, it is impossible to obtain good results with certainty and uniformity; and it is generally necessary to add acetate of silver to

the bath, in order to obtain sufficient density in the blacks. When the nitrate of silver is pure, and nearly all the free nitric acid got rid off by redissolving and recrystallizing it, the bath works well without any additions. It gradually acquires silver iodide, potassium nitrate, and organic impurities by use.

It may be remarked that by leaving the plate in the bath longer than is requisite, and when the collodion is tender, or has been introduced before it has sufficiently dried and acquired proper tenacity, it frequently cracks and drops in fragments into the bath. If the collodion be good and moderately old, the excited plate possessing an opal hue suffers no injury by remaining a little longer immersed; but when the bath is fresh, it should be taken out as soon as it becomes sufficiently excited, otherwise the iodide on the plate will be attacked. Such an inconvenience may be obviated by iodizing the bath in the first instance, allowing a collodionized plate to stand in it for a quarter of an hour. Another plan is that of introducing iodide in the bath on its preparation, making up the solution according to the following formula:—

Nitrate of silver,	1 oz.
Distilled water,	14 ozs.
Iodide of potassium,	½ grain.
Nitric acid,	1 drop.

The addition of a trace of nitric acid prevents the plate from fogging. The operation of exciting the plate must take place in the dark.

To keep the negative bath in good order is one of the first axioms of photography, for unless the exciting solution in which the plates are dipped is perfectly free from foreign matter, it will be impossible to secure good results. After a time, naturally enough, the best bath will become contaminated with both chemical and mechanical impurities, and the only course to be adopted is to thoroughly purify it again, or, what is perhaps the best plan after all, throw it into the residue tub, when the silver it contains is precipitated and collected. It is always well to skim one's bath every morning before use with a clean bit of filter paper, for in this way any particle of dust and other matter floating upon the liquid is removed, and does not attach itself to the film as soon as the first plate is immersed. Sunning the bath frequently in full daylight, and then filtering it, is a good way to remove organic matter, or a few drops of a weak solution of permanganate of potash may be added with a like result. Fogging of the image is generally prevented by the adding of a drop or two of nitric acid, so that the liquid when tested with blue litmus paper turns the same slightly red. Pinholes on the plates, arising from too large a quantity of iodide of silver in the bath, may be obviated by adding a further instalment of nitrate of silver dissolved in distilled water.

It has often been pointed out, and among others by Captain Abney in the "Year-book of Photography," that the methods usually in vogue for turning old baths into new ones do not generally rid the solutions of the whole of their impurity; and the cadmium, potassium, and other salts, contracted from the collodion, are invariably left behind. By boiling down a bath to dryness and fusing the silver, the nitrate of silver is freed from organic matter and the ammonia salts. By precipitating the silver as carbonate, the ammonia salts, and perhaps the potash, are eradicated; but in both cases the cadmium salts are left, and either organic matter or potash salts are left, so that when the fused mass is redissolved, the negative bath is still impure. Captain Abney recommends two methods of treating old baths. In both cases permanganate of potash should be added to the bath to destroy organic matter till a faint tint is formed in the solution; next add a quarter the bulk of water, which will cause an emulsion of iodide of silver, and filter; take one-twentieth of the whole, and add a solution of caustic potash to a portion. This will precipitate the silver as oxide of silver. Wash well in a filter till the droppings, when burnt on cotton wool in a flame, show no violet flame when looked through blue glass. Should this test not be available, let four filters full of water pass through the oxide. This will suffice. Place the filter paper on a dish near the fire, so that the excess of moisture is drawn off, and the oxide may be detached from the paper. Thus far the plan of operating is similar in both methods.

First Method.—In the filtered-bath solution place strips of copper or copper-wire, and leave them undisturbed for twenty-four hours. This will throw down the silver in a metallic state, leaving the nitrates of copper and cadmium and potassium in solution. Take two or three drops of the solution, and test for the absence of silver by adding a little solution of common salt to them. If no white precipitate appear, the conversion into metallic silver is complete. Carefully decant the supernatant fluid, and withdraw all the copper visible; wash the silver in three or four changes of water until the blue colour due to the nitrate of copper is absent; all the other salts will be washed away with the nitrate of copper. Place the metallic silver in a large porcelain dish, and add *gradually* 1 drachm of pure nitric acid (1·36, the strength of the British Pharmacopœia) to every 150 grains of nitrate of silver in the original bath solution. The silver will gradually dissolve, and will be much aided if heat be applied. The solution will now have a greenish colour, from small particles of copper which have fallen from the original wires or strips, and which have become coated over with metallic silver. These small particles of silver will be dissolved by the nitric acid, and will form nitrate of copper. Boil down the solution to small bulk, till it begins to spurt. This will free it of any great excess of nitric acid. Next add distilled water to it till it has a slightly larger bulk than it had before boiling down; next add the oxide of silver, little by little, till the blue or greenish colour has entirely disappeared. This will precipitate the oxide of copper from the nitrate of copper, setting free the nitric acid, which in its turn will combine with the oxide of silver. The copper will fall as a black powder, mixed with any excess of

oxide of silver there may be. Take one or two drops of the solution in a measure, and add a drachm of water, and then add ammonia to it till the precipitate first formed is redissolved. If no blue colour is apparent, the substitution of the silver for the copper is complete; if not, more oxide of silver must be added till the desired end is complete. Distilled water must next be added till the strength of the bath is that required. This can be tested by the argentometer. An emulsion of iodide of silver may here appear; if it does, no matter. When the solution is filtered the bath is fit for use, being chemically pure, neutral, and charged to a proper extent with iodide of silver.

Second Method.—After the bath has been diluted, add a little of the oxide of silver till there is no residue left. This will leave the bath in a strictly neutral condition; filter, and to it add a saturated and filtered solution of ferrous sulphate (perfectly clean crystals should be used); about a quarter of an ounce of iron to every 10 ozs. of bath should be prepared. The silver will be precipitated in the metallic state. It should be filtered and well washed with water, till the droppings from the filter show no signs of a red colour on the addition of sulphocyanide of potassium, or a blue tint with cyanide of potassium. The silver may now be placed in the porcelain dish, and nitric acid added as before. The oxide of silver must be added till there are a few grains left unattacked by the free nitric acid. The solution is then diluted to proper strength, and the bath after filtering is fit for use. The superfluous oxide may be converted into nitrate of silver by adding nitric acid to it, leaving a few grains intact. This may be diluted to the proper strength, and after filtering added to the new bath.

These may appear rather complicated methods of treating an old bath to make it do duty as a new one, but it is only by a very careful and thorough operation that the desired transformation is possible. If a photographer uses a good deal of silver solution for printing, it is a far wiser course to employ old dipping baths for sensitizing paper. This is not, however, always possible, for carbon printing is coming so much into vogue that silver is employed in no other branch of photography than in the negative process. Under these circumstances, should the operator fail to succeed in transforming his old bath into a good servicable solution again, he has no alternative than to throw it into the residue tub—a large earthenware pan containing some salt, or crude muriatic acid in solution, to bring down a precipitate of chloride of silver. In nine cases out of ten this is indeed the best thing to do with old silver solutions, unless, as we have said before, they can be employed for exciting paper for printing purposes.

These residues may be sent to a refiner, who will give a fair equivalent value, or the photographer may reduce them himself if he has a furnace and crucibles at his disposal. (See *post*, Recovery of Waste Silver and Gold in Photography.)

The Exposure in the Camera.—This is a point on which it is impossible to give exact directions; but the faults due to over and under exposure may be clearly pointed out. In an under-exposed picture the details of the shadows cannot be brought out, and the blacks acquire excessive opacity. In an over-exposed picture the details of the shadows appear before the blacks have had time to become sufficiently intense; and since the development cannot then be sufficiently prolonged, the result is a flat feeble picture, deficient in contrasts.

The proper time of exposure depends on the aperture of the lens and its focal length, and varies directly as the square of the focal length, and inversely as the square of the diameter of the aperture, when different lenses are employed. By the focal length is meant the distance of the focus, or point of convergence of the rays, from the centre of the lens; that is, the distance at which the image on the screen appears quite distinct.

To Develop the Latent Image.—Hold the plate in the left hand by one corner, or place it upon a levelling stand, and pour over it a sufficient quantity to cover it, of either of the following mixtures:—

	Hunt's.	Delamotte's.
Pyrogallic acid,	1 grain	5 grains.
Water,	1 oz.	10 ozs.
Glacial acetic acid,	1 scruple	40 drops
	3 ozs.	2 drachms.

Or better still—

Sulphate of iron,	½ oz.
Glacial acetic acid,	½ "
Alcohol,	½ "
Water,	8 ozs.

In a minute or less the dark parts of the image appear, and are soon followed by the half tones and finer details in the shadows. Let the developer flow backwards and forwards over the plate until the picture is fully out and sufficiently dense. If the collodion is good, and the nitrate bath in good order, the development need not be hurried, but may occupy several minutes. Under some circumstances it may be well to add a few drops of solution of nitrate of silver to the developer in a measure, and pour it again over the plate, in order to give the blacks greater intensity.

When the negative is fully out in all its details, wash it well with water.

To Fix and Finish the Picture.—When the plate has been well washed after the development, by pouring water over it from a jug, the yellow iodide of silver should be dissolved out by means of either a saturated solution of hyposulphite of soda, or a solution of cyanide of potassium; strength about 5 grains to the ounce of water. This should be poured over the plate, and should be allowed to run backwards and forwards over it until the whole of the yellow iodide of silver in the plate has disappeared; after which it should be thoroughly well washed, by pouring water over it from a jug, and set up to drain and dry; or it may be dried before a fire. It is then ready to be varnished.

The best kind of varnish for a cold plate is made by dissolving powdered dammara resin in benzene. This is poured over the picture in the same way as

the collodion on the plate. It dries in a few minutes. But a better varnish, used with a heated plate, is made by dissolving shell-lac in alcohol. This is called spirit varnish. Before applying it, the plate should be heated before a fire to about 100° Fahr. (37°·7 C.); and after applying it, to about 150° Fahr. (65°·5 C.). When dry this varnish is extremely hard, and protects the picture effectually from injury in printing.

The negative is now finished. An unlimited number of prints may be taken from it by the printing process.

The Positive Collodion Process.—A collodion negative is intended to be looked through; a collodion positive to be looked at. A negative must possess density when looked through, and the colour of the surface deposit is of little consequence. A positive need not possess density when looked through, and the colour of the surface deposit is of great consequence, for it should be white. Hence the difference between the processes. Now it is found that organic matter combined with the silver of the images gives density and a bad surface colour; while the absence of organic matter gives a good surface colour, but no density. It is evident, therefore, that in the positive process an inorganic developer, such as the sulphate of iron, must be used instead of pyrogallic acid, which is an organic substance; while the nitrate bath should be acidified with nitric, and not with acetic acid. Bearing these things in mind, the processes become nearly identical in manipulation; the only difference being, that in the development of positives, the operation is much quicker, since it is only a superficial indication of detail that is wanted, and not density.

A positive is true to nature, because wherever the light acts metallic silver is precipitated; while the parts where light does not act remain clear glass, and these are converted into dense blacks by simply applying black varnish to the back of the glass.

The nitrate-bath for positives is composed of—

Distilled water,	1 oz.
Nitrate of silver,	35 or 40 grains.
Nitric acid,	1 minim.

The developer is made thus:—

Ferrous sulphate,	100 grains.
Glacial acetic acid,	½ oz.
Water,	10 ozs.
Nitric acid,	5 minims.
Alcohol,	½ oz.

The development of a positive only occupies a few seconds, and must be stopped as soon as there is the faintest indication of the details in the shadows. The plates should then be well washed to remove all traces of iron, and the picture fixed with a liquid composed of—

Water,	60 parts.
Cyanide of potassium,	6 "
Nitrate of silver,	1 "

The picture should be fixed with potassium cyanide, and not with hyposulphite of soda, for two reasons: first, because the cyanide removes more perfectly any organic compound of silver which might injure the colour of the picture; and secondly, because the hyposulphite of soda injures the colour by blackening the silver.

A black ground may be given to the picture, either by backing the plate with velvet, or by pouring upon it black varnish. This is made by dissolving asphaltum in benzene, and adding a little india-rubber to prevent it from cracking, a fault to which it is very liable. Printers' ink makes a good varnish, which does not crack. To apply it, rub it upon the back of the glass, and also upon a piece of paper, and then press the blackened side of the paper against the blackened side of the glass, and put the picture at once into its case. Collodion positives should always be taken in a non-reversing slide.

Positive pictures may be obtained from negatives in a variety of ways. Fry, after developing the images with the ferrous salts as above described, changed the negative to a positive by pouring upon it a mixture of pyrogallic acid and hyposulphite of soda which had undergone partial decomposition, and warming gently. By this treatment the darkened parts are rendered brilliantly white from the formation of metallic silver. Archer pours a mixture of 1 part of a saturated solution of protochloride of mercury, acidulated with hydrochloric acid and 6 parts of water, upon one corner of the plate, and allows it to flow over the fixed negative picture. At first the shades are deepened, but quickly the appearance alters, and a very delicate white picture results. This picture may be changed from positive to negative, and *vice versâ*, by applying ammonia and the mercurial compound alternately.

Dry Collodion Process.—Spiller and Crookes were the first to suggest a method of preserving the sensitive collodion film after it had been excited in the silver bath, and Dr. Norris, Fothergill, and Paupenot followed soon afterwards with various processes to the same purpose. All the plans suggested by these gentlemen are now obsolete, but many of the dry-plate processes practised at the present day are indications of the earlier methods. Of late years dry-plate photography has become exceedingly important, having reached a high state of perfection, and presenting in some respects great advantages over the ordinary wet process.

The collodio-albumen process employed by W. England is one of the simplest methods of preparing dry plates. After the glass has been thoroughly cleaned, it is coated in the ordinary way by bromo-iodized collodion of any good maker, and sensitized in a 40-grain nitrate of silver bath. It is then washed with distilled water, or good rain water, until all greasiness has disappeared; and then plain albumen, to which a few drops of ammonia have been added, is poured over the film. In hot weather 1 part of white of egg to 3 parts of water answers better; the albumen is beaten to a froth, allowed to subside, and decanted before use. The albumen is flowed over the film several times and then poured off, and the film washed under a gentle stream of water.

The next thing is to sensitize this thin film of albumen covering the collodion; this is done by pouring over it a 30-grain solution of nitrate of silver, to which a few drops of acetic acid have been added. In summer, when diluted albumen has been employed, a 5-grain solution is used, with a little acetic acid. This restores the sensitiveness of the film, and the plate should then be thoroughly washed and placed to dry. By employing a fresh solution for every sensitizing, each plate is obtained in the best possible condition and of precisely the same quality.

A convenient article for washing dry plates may be easily made. Procure a small india-rubber tube, and pass one end through an American clip, a hole having been made in one of the pans of the clip for the purpose. Allow the pipe to pass through about 3 inches. To the end of the tube attach a rose; those sold for drawing-room fountains answer perfectly. In this way a very useful article may be made, for by pressing the clip a soft shower of water may be thrown upon the plate. The tube may be attached to the tap of any vessel containing water.

These plates should be exposed three or four times as long as a wet plate. To develop, place the plate on a levelling stand, and moisten the surface with water. Afterwards pour over a solution of pyrogallic acid, of the strength of 2 or 3 grains to the ounce of water Allow this to remain until details are fully out, or a faint red image shows itself. Now proceed to intensify with either pyrogallic or citric acid, or pyrogallic and acetic acid. The latter is to be preferred, but the former is probably better in warm weather. Fixing may be undertaken either with hyposulphite of soda or cyanide of potassium (see *post*, Alkaline Development).

As regards collodion, it should be employed of two kinds—one prepared with 3 grains of bromide to 3 of iodide, and a second with 1 grain of bromide to 4 of iodide, to each ounce of collodion. With a view to presenting very great contrast of light and shade, a fine soft picture, full of detail in the shadows, can be obtained by using the collodion containing the larger proportion of bromide. On the other hand, working in an unfavourable light, and on a subject presenting but little contrast, a more vigorous negative can be obtained by decreasing the bromide.

Russell Manners Gordon's gum process is as follows:—A good collodion and a 40-grain nitrate of silver bath are chosen. The plates having been cleaned and coated with a preliminary film of albumen, or india-rubber in benzene, are collodionized and placed in the bath for not less than ten minutes. They are then washed in two baths of distilled water, and subsequently under the tap. The film is finally swilled with distilled water, and the plate flooded with a 3-grain solution of gallic acid; drain off, and apply the preservative, freshly prepared, viz.,—

Gum arabic,	20 grains.
Sugar candy,	5 "
Distilled water,	1 oz.

Filtered through a sponge; dry the plates carefully. These plates are almost as sensitive as wet.

The Collodio-bromide Dry Process, which has been worked out by Messrs. Sayce and Bolton, Carey Lea, H. Cooper, Colonel Stuart Wortley, and others, consists in the formation of an emulsion of bromide of silver in collodion, with an excess of nitrate of silver. Colonel Wortley recommends the addition to the bromide emulsion of 2 per cent. of nitrate of uranium; and certainly the Wortley dry plates, as prepared commercially, leave very little to be desired. The uranium, according to Colonel Wortley, adds to the preservative qualities of the plates, and renders them more sensitive.

The Collodio-bromide Method, given by Henry Cooper in the "Year Book of Photography," is also a very good one, especially when great sensitiveness is desired; only it must be borne in mind by experimenters, that the more sensitive they may use their plate, the more care they must use to exclude daylight, and to avoid stains, &c., from want of cleanliness. After the glass plates have been thoroughly cleaned, they receive a preliminary coating, or substratum, to render the collodion more adhesive to the glass. Either a weak solution of india-rubber in chloroform, or albumen diluted with about five or ten times its bulk of water, may be used. If a large proportion of gum is afterwards applied as a preservative, the india-rubber solution is better; but for the salicine preservative, or one in which there is little or no gum, albumen is preferable. The bromo-chlorized collodion is made up of—

Anhydrous bromide of cadmium,	52 grains.
Anhydrous chloride of cadmium,	8 "
Alcohol, ·805,	2½ ozs.
Pyroxylin,	45 grains.
Ether, refined methylated,	4½ ozs.

Those who do not care to prepare the collodion for themselves may obtain it from Manson & Swan, of Newcastle; the pyroxylin employed is that manufactured at a high temperature.

An emulsion is next formed by placing 14 grains of powdered nitrate of silver in a small glass flask; to this is added 7 minims of distilled water, the solution being facilitated by heat. Pour in afterwards 3 drachms of absolute alcohol, and warm again over the spirit lamp until all the nitrate has been taken up. If the silver is precipitated from the aqueous solution on the addition of the alcohol, it matters little, and the application of heat a second time causes the alcohol to take up the precipitated salt again. Whilst the solution is still warm, add it gradually to 7 drachms of the bromo-chlorized collodion, previously measured into a clean and dry-stoppered bottle. The only precaution to be observed is, to add a very little of the nitrate solution at a time, shaking violently between each dose. If an assistant will do the shaking, the operation is much simplified, as the flask of silver need not then be put out of the hands. Finally add 5 drops, not minims, of syrupy lactate of ammonia. The emulsion may be used in about twelve hours, but gains in sensitiveness by keeping somewhat longer. The quickest plates are made with an emulsion prepared

as follows:—10 drachms are sensitized as directed above; and after standing two days, 7 drachms of bromo-chlorized collodion are added; and after well shaking, it is fully sensitized with 14 grains of nitrate of silver dissolved in 3 drachms of alcohol, and 5 drops of lactate finally added. The plan of adding fresh emulsion to the old may, of course, be adopted with any residues left after preparing a batch of plates.

After coating with emulsion, the plate is rinsed in two changes of distilled or soft water, until the greasy lines disappear, and is then soaked for two minutes in a bath or dish of the preservative, and then drained and dried perfectly. Either of the two under-mentioned preservatives may be employed; they will keep good a long time, and may be used over and over again with occasional filtration. For either of them two stock solutions are required, viz., a 60-grain solution of tannin in water, to which a little carbolic acid is added; and secondly, a 48-grain solution of gallic acid in alcohol. The tannin solution should be cleared by filtration or decantation; and if it cannot be obtained quite bright in this way, the sample of tannin should be rejected.

Preservative No. 1.

Sugar,	50 grains.
Gum,	50 "
60-grain solution of tannin,	1 oz.
48-grain solution of gallic acid,	½ "
Water,	9 ozs.

Preservative No. 2 (Colonel Wortley's Salicine).

Saturated solution of pure salicine in distilled water,	2 ozs.
60-grain solution of tannin,	1 oz.
48-grain solution of gallic acid,	½ "
Sugar,	40 grains.
Water,	7 ozs.

The development of these plates, which may take place weeks afterwards, should be conducted by means of an alkaline developer (see *post.*, Alkaline Development).

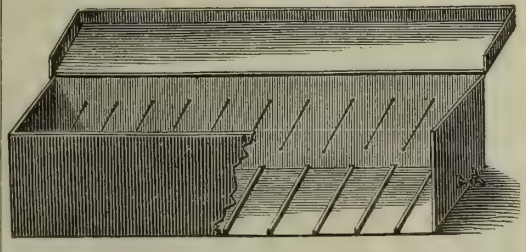
M. de Constant's albumino-gallic dry process is the result of many years' experience of dry plates. M. de Constant of Lausanne has been from the commencement a most busy dry-plate worker, and has elaborated many working details connected with the process which are of value. His improved process, as it now stands, is as follows:—Good clear glass plates are well cleaned by boiling in a solution of common soda in the proportion of ¼ lb. of the latter to 8 litres of water, and afterwards, when the solution is cold, the plates are taken out, washed under a tap, and rubbed with the hand; they are then stood on end upon blotting paper and allowed to drain, and finally rubbed dry with the same paper. They are coated with a solution of albumen—the white of an egg being beaten up into froth and allowed to subside, and added to 25 volumes of water with a couple of drops of ammonia, and filtered—the solution being poured on the plate and spread by means of a glass rod. (Care should be taken that the rod is scrupulously cleaned after the coating of each plate.) The plates are put on end on filter paper, and in a couple of hours are perfectly dry; they may then be coated at once with collodion, or stored away in boxes for use when convenient.

The collodion employed should be made of pyroxylin prepared at a high temperature, so as to give a porous film, iodized in the ordinary manner; but when landscapes, or pictures with strong contrasts, are to be reproduced, it is always well to add 1 gram. of bromide of cadmium for every 240 grams. of collodion, as the plates are thus rendered more sensitive and more detailed in the shadows. A little stale or red collodion may be added with advantage. The sensitizing bath should be made up with good recrystallized nitrate of silver, 500 cubic centimètres of distilled water being employed to dissolve 40 grams. of the nitrate; one or two drops of pure nitric acid are afterwards added until blue litmus paper indicates an acid reaction. The bath must be kept pure by frequent sunning and filtering, and should be tested by a wet plate before being employed in the preparation of dry plates.

An albumenized plate is coated with collodion and dipped into the bath at one stroke, the plate being moved up and down once or twice, and then allowed to rest. In about three minutes, if all signs of greasiness have disappeared, the plate may be taken out, and is then plunged into a bath of distilled water, to which a few drops of acetic acid have been added, and here it remains while a second plate is being sensitized. The first plate is now taken from the bath and put under a soft stream of ordinary water from a rose, and placed on end in a trough of water until the end of the operation, and a sufficient number of plates have been prepared. Of course, no white light must be allowed to enter during all these manipulations.

In this trough the plates are allowed to remain for a couple of hours; strips of metal about half an inch high soldered at the bottom of the trough prevent the plates from slipping, while wires or other strips of metal near the top serve to rest the backs of the plates against (see Fig. 12).

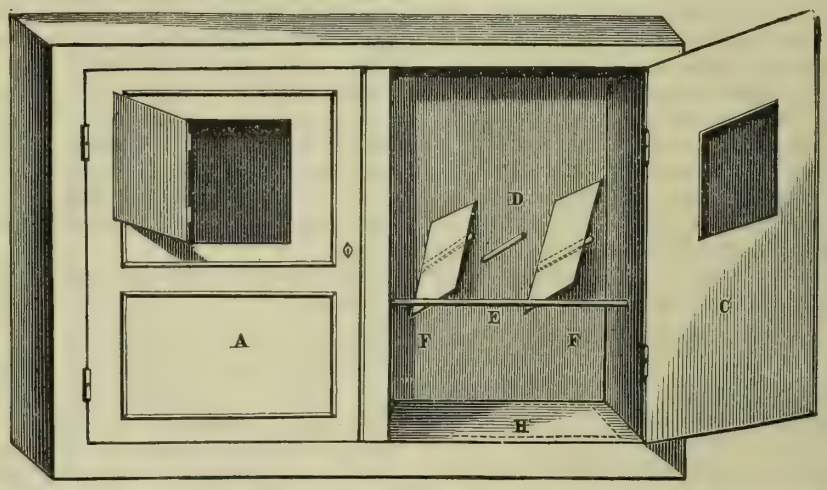
Fig. 12.



The preservative for covering the plates is prepared as follows:—The white of one egg, after separating the germ, is put into a vessel with 10 cubic centimètres of water, and whipped to a froth with a wooden fork. After standing some hours 4 cubic centimètres of the liquid is shaken up in a bottle with 140 cubic centimètres of distilled water, and ½ gram. of gallic acid and 2 grams. of pow-

dered caramel added. The mixture is agitated for about a quarter of an hour, and the dissolution is then complete; it is then filtered twice through white filter paper. The resulting liquid is limpid, of a brownish colour, containing 35 parts of water for every part of albumen, and it should be employed fresh. When the prepared plate is taken from the trough a small quantity of the preservative is poured on and off, and then a second is applied, which remains on the collodion film for about a minute; the liquid must not be allowed to fall in a stream from very high upon the plate, otherwise bubbles will be produced. The plates are drained as before, and then put into a drying closet, for it is very important that the films should be well and uniformly dried. The drying must not take place too rapidly, but should be of an even nature, and if carried out successfully the film is perfectly dry and brilliant, without any spots or markings when seen by transmitted light. The best method of drying is

Fig. 13.



to have a drying cupboard placed in a room warmed to a moderate temperature. The cupboard is shown in Fig. 13; A is the cupboard closed, with window open; B, the yellow tammy stretched over window; C, cupboard open; D, pegs for leaning the plates against; E, lath cut to a knife edge upon which the plates rest; F, little strips of paper attached to plates for draining them; H, sheets of filter paper to receive draining from the plates.

Many kinds of dry plates require to be backed by some pigment to prevent blurring, the transparent nature of the film allowing the light to pass through too freely. This is not necessary in this case, for the tint of the caramel renders the film opaque. The development of these plates, after exposure, is carried out with an alkaline developer (see *post.*, Alkaline Development).

As dry plates are usually employed by travelling photographers, it is very necessary that on the journey they should be packed in light-proof packages, and safe from the action of a damp atmosphere. Gordon recommends separating the plates by placing between them a guard made by pasting two strips of cardboard longways down a piece of ribbon, and thus making a hinge, in which the plates rest as in a groove, Fig. 14. Another plan is to separate them by sheets of thin cardboard, of which the middle has been cut out, so that only the margins of the plates are touched by the card, Fig. 15; but any simple contrivance will answer, such as can be adjusted in the dark, for so sensitive are the dry plates of the present day, that a candle flame is sufficient to injure them. In packing they should be enveloped in a moderate temperature, so that heat and cold will have little effect upon their surfaces when in the dark slides; and if the backs are covered with a pigment of any kind, they must be separated from each other, as otherwise the colouring matter will become detached and adhere to the films. First a layer of red or reddish-brown paper should envelop the plates, and then a covering of brown paper, tarred on one side to render it water-proof, is used. Packing subsequently in two sheets of tin foil will sufficiently protect the films from damp and dust, and also from the clammy sea air during a short voyage. The first sheet of tin foil should be thin, and the second thick (caddy tin); and fresh sheets should be employed when the plates have been exposed, and they are to be taken home for development, as the thin material easily becomes torn. The caddy tin is very suitable, as it bends and does not break easily. Before putting the plates into the slides for the day's work, wipe carefully the inside of the slide; also brush lightly with a soft silk handkerchief or broad camel's hair brush

Fig. 14.

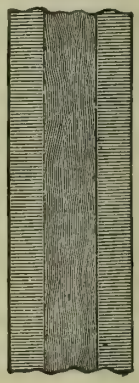




Fig. 15.

the sensitive films, so that no specks of dust remain upon the surface, which would otherwise produce defective negatives.

Alkaline Development.—Colonel Stuart Wortley, who has paid considerable attention to the subject of dry plates and their development with an alkaline liquid, recommends the experimenter to make himself well acquainted with the principles and practice of alkaline development, as upon it rests in a great measure success in dry-plate photography. As regards his mode of development, which is given below (and which, although more especially fitted for uranium dry plates, prepared according to his own formula, may nevertheless be employed with nearly every kind of dry plate), pyrogallic acid and ammonia are the active agents, while bromide is used as a restrainer, replacing in this process the acid used in the wet. The pyrogallic acid should be used always in the same proportion, and the ammonia and bromide varied according to circumstances. Colonel Wortley says, if a plate fogs, it is due to one of three causes—1st, from extraneous light having got at the plate in some way; 2nd, from over-exposure; and 3rd, from the use of too little bromide in the development. These errors are easily guarded against, and experience soon enables one to detect faults in manipulation. Should the dark shadows remain too clear and deficient in detail, it is a sign that the plate is under-exposed, or that too much bromide has been used in the development. One noticeable point in treating plates in this way is the advantage they have over wet plates in the latitude permissible in their development; so that if you know they have been over or under exposed, you may remedy the fault in a great measure by altering the proportions when mixing the developer. Thus, if two plates are exposed at the same view at the same time, one for five seconds and the other for fifteen, and the first is developed with a solution containing ammonia, 30 drops, and bromide, 20 drops, and the second with a solution containing ammonia, 30 drops, and bromide, 30 drops, the resulting negatives will be as nearly as possible identical; but if you were to reverse the developing solutions on the two plates, you would infallibly spoil both. The one exposed five seconds would be useless, because the short exposure and the bromide in the developer would both act in preventing sufficient detail in the shadows; while the other negative would fog, having had a long exposure, and not sufficient bromide being used to control the development. If the experimenter bears this in mind, he will soon obtain the necessary experience for maintaining a correct balance between the exposure of the plate and the proportion of bromide and ammonia. Plates that have been sufficiently exposed can be developed quickly, and will attain sufficient density without redeveloping with silver. Plates that have received a short exposure, such as skies, instantaneous views, portraits, &c., require to be slowly and patiently developed, in order to obtain the best results. With such subjects it may occasionally be found undesirable to complete the development with ammonia, but to attain density by, after intensification with pyro and silver, stopping the ammonia development when the detail is quite out. The following solutions will be required:—

A	Carbonate of ammonia,	64 grains.
	Water,	1 oz.
B	Bromide of potassium,	4 grains.
	Water,	1 oz.
P	Pyrogallic acid,	96 grains.
	Pure alcohol,	1 oz.
M	Methylated spirit,	—
W	Distilled water,	—

Should there be any difficulty in obtaining carbonate of ammonia, ordinary liquid ammonia will answer the purpose, used in the following proportions:—

Ammonia,	20 drops.
Water	1 oz.

The carbonate is, however, far preferable.

To proceed with the development: put the exposed plate on a levelling stand, and pour over it alcohol of ·825 strength, diluted with 20 per cent. of distilled water, and leave it to soak into the film for about a minute, during which time you can mix your developing solutions in the following manner:—Take 4 drachms *W* and 1 drachm *M*, add 5 drops of *P* and 30 drops each *A* and *B*; pour the alcohol off the plate back into its bottle, and wash the plate thoroughly under a tap till the greasiness of the alcohol is washed from the surface; if there is any backing or pigment on the plate, wash this off with a sponge or with your hand. Pour the developer on to the plate, running it along the edge and over the plate with an even sweep; keep pouring off and on, and the negative will rapidly come up, adding more ammonia from time to time to bring up the density and detail, adding about half the quantity of bromide with it each time, with the view of keeping the shadows clear. The first alcohol can be used over and over again, but will want filtering. Those to whom alkaline development is quite new will do well to begin by using the developer diluted with water.

According to the way in which the plate comes out, you will see whether the exposure and development have been right; if the plate flashes out at once on the application of the developer, it is over exposed, and more bromide should be added at once to control development. If, on the contrary, the negative remains for thirty or forty seconds without the picture appearing, it is a sign of under exposure, and from 10 to 20 drops of *A* may be added to the developer. It may be that some pictures taken in a weak light may require much forcing; if so, remember to add the same proportions of *B* with *A*. If the plate is very clear and devoid of detail, it may be well to add a few drops of *A* without any *B*. Bear this rule ever in mind: if you wish the plates to work more quickly, reduce the bromide in the developer; if there is any tendency to fog, increase the bromide or decrease the exposure. On any dark spot in the picture where there is a deep shadow

pour the solution constantly, which will soon bring out the detail. It is frequently very useful to pour the developer off the film, and leave the negative on the developing stand with no solution on it for a minute or two at a time, as that assists to bring out both detail and density. In pouring off the developer, rock the plate so that the former does not run in lines. When plates appear under-exposed, and the first developer has exhausted its action, make up a second quantity, adding 4 drachms of water, 10 drops of *P*, 30 drops of *A*, and 20 drops of *B*, and continue to add *A* freely with the same proportion of *B* till the negative is finished. If sufficient density is not secured by this development, then the plate is washed well, and treated with a solution of acetic acid or citric acid in water—about half a drachm of the former or 2 grains of the latter to the ounce of water; leave this on the film for a couple of minutes, and then wash thoroughly off and fix in a solution of—

Hyposulphite of soda,	1 oz.
Water,	8 ozs.

Or,

Cyanide of potassium,	20 grains.
Water,	1 oz.

After mixing, wash thoroughly, and make a solution of—

S	Nitrate of silver,	10 grains.
	Nitric acid,	20 minims.
	Water,	1 oz.

Take 20 drops of *P* in half an ounce of water, and add 10 drops of *S*, which pour on and off till the desired intensity is obtained. The intensifying can be done before fixing if desired, taking care to use the acid before employing the intensifier; or the negative can be fixed and allowed to dry, and remoistened and intensified at any time afterwards. More recently Colonel Wortley has advocated the employment of a more powerful alkaline developer than the one above specified.

Another plan is that advocated by Messrs. Manson and Swan, which is recommended by M. de Constant and others. Three solutions are made:—

No. 1.	Alcohol,	30 c.c.
	Pyrogallic acid,	4 grams.
No. 2.	Distilled water,	30 c.c.
	Carbonate of ammonia,	1 gram.
No. 3.	Distilled water,	40 c.c.
	Bromide of potassium,	1 gram.

The plate, after exposure in the camera, is put into a bath of water, where it remains for a minute or two, and it is then passed under a rose; if the negative is full-plate size, 30 c.c. of water are added to 20 or 30 drops of No. 1 solution, and poured upon the film to completely soften it. This liquid is moved to and fro on the plate for a couple of minutes without producing any image. It is then poured off again into the developing cup, and there is added 10 drops of No. 2 and two or three drops of No. 3. This mixture thrown upon the plate at once produces an effect, and a picture is produced rarely requiring any subsequent intensifying with silver. If the details do not readily appear, a few more drops of No. 2 are added; or a second mixture of the solutions may be employed, in which the proportion of No. 3 (bromide) may be reduced, or omitted altogether. If a sufficient exposure has been given, the development should be completed in five minutes. Should the image lack vigour, it is intensified with a weak solution of pyrogallic and citric acid in water, to which a few drops of a 3 per cent. solution of nitrate of silver have been added. A thorough fixing of the plates must not be forgotten, the film, having once dried, requiring longer treatment with the fixing solution than an ordinary wet film.

Instantaneous Pictures.—The production of so-called instantaneous photographs depends for the most part on a quick acting lens, an energetic developer, and a good light. Any rapid lens of short focus will answer the purpose, and with a large aperture it is sometimes impossible to cap and uncap the lens with sufficient rapidity. Some photographers employ instantaneous shutters, to be lighted by a turn of the wrist; others prefer to employ a dark cloth, or a bit of velvet; and others again have an arrangement with a spring and trigger for giving very brief exposures. The plates must be cleaned with more care than usual, because marks which would produce but slight stains in ordinary work become very apparent on using a strong developer. Dry plates have now reached such a state of perfection that some descriptions—the collodio-bromide, for instance—may be employed for this work. In this case a very strong alkaline developer must be employed, similar to the one specified under the paragraph of Alkaline Development, but with more ammonia added. In the wet process the collodion should, of course, be of first-class quality and in ripe condition, but that of nearly every well-known maker will serve. The dipping bath must be slightly acid, the plates being left therein for the usual period. Elwell, who has been very successful in this branch of the art, uses a developer for wet plates made up according to the following formula:—

Amm. sulph. of iron,	1 oz.
Sulph. copper,	1 dram.
Nitr. potash,	1 "
Water,	12 ozs.
Glacial acetic acid,	½ "
Liquor ammoniæ,	3 drops.
Alcohol,	Quant. suff.

In development you must work rapidly and with judgment, and the plate should be intensified, if it requires it, both before and after fixing.

Colonel Stuart Wortley makes his developer as follows:—

Sulphate of iron,	20 ozs.
Distilled water,	120 "
Dissolve.	
Acetate of lead,	½ oz.
Water,	5 ozs.
Dissolve.	

Mix the above solutions, and when the precipitate has all settled, decant off very carefully. Add—

Formic acid,	5 ozs.
Acetic acid,	1½ oz.
Nitric ether,	1½ "

This is kept as a stock solution, and as much as is required for use is filtered off and acetic acid added in proportion, according to the temperature of the weather and the class of picture required. Colonel Wortley recommends intensifying after fixing, pouring on a saturated solution of bichloride of mercury, and after a good washing, a 5-grain solution of iodide of ammonium in water. Then two solutions are used, composed of—

No. 1.	Pyrogallic acid,	12 grs.
	Water,	1 oz.
No. 2.	Citric acid,	50 grs.
	Nitrate of silver,	10 "
	Water,	1 oz.

Pour a few drops of No. 2 into No. 1, and pour on and off the film. The negative can be made to assume any desired depth.

Micro-photography.—One of the most successful micro-photographers is Dr. E. J. Gayer, who has succeeded in depicting instantaneously animalculæ alive in water. He employs a large compound microscope in connection with his camera; the former is placed horizontally, the eye-piece end being slid into a short brass tube screwed into the front of the camera. He employs a one and a half inch object-glass, and an *A* eye-piece; and the difference in the magnifying power he obtains by altering the distance between the object-glass and the eye-piece, and by increasing or diminishing the distance between the eye-piece and the photographic plate. Dr. Gayer uses either direct sunlight reflected from a plane mirror, and if the objects are semi-opaque, he illuminates the surface by reflected light, as otherwise surface-markings would not be shown. If he requires to work instantaneously he employs a suitable shutter which will not cause the instrument to vibrate. A good strong light, a sensitive collodion, and an active developer, is all that is needed.

Theory of the Collodion Processes—The sensitive collodion film is composed of iodide of silver, free nitrate of silver, and collodion. The iodide of silver is formed by immersing the iodized collodion film in the bath of nitrate of silver, so that iodide of potassium, plus nitrate of silver, becomes iodide of silver, plus nitrate of potassium.

The collodion in the above equation appears to have a retarding effect on the action of light, because when a mixture of iodide of silver and nitrate of silver alone is exposed to light, it darkens more rapidly than when collodion is present. The collodion must not, therefore, be considered as an accelerator, but as the vehicle for supporting the sensitive chemicals upon the glass, and forming with the reduced silver an opaque compound in the darker parts of negatives. In the development of the picture, the pyrogallic acid accelerates the reduction of the silver salts on those parts on which the rays of sunlight have fallen, producing finely-divided metallic silver, which constitutes the blacks of the negative. The acetic acid, added to the pyrogallic developer, prevents its spontaneous or too rapid decomposition when mixed with the nitrate of silver. When, in the development of a positive, ferrous sulphate is used instead of pyrogallic acid, the difference between it and the organic acid mentioned is attributable to the fact, that it does not reduce as much of the metal as the latter; consequently the precipitate is thin and transparent, and looks white when viewed by reflected light.

When potassium cyanide is used to fix the picture, that is, to remove the silver iodide, it has but little action on the image, while it decomposes the iodide of silver, and forms a soluble double cyanide of silver and potassium, together with potassium iodide. When hyposulphite of soda is used, the iodide of silver is decomposed, and the products are a soluble double thiosulphate of silver and sodium, together with sodium iodide.

The Albumen Negative Process upon Glass.—To prepare the albumen collect in a basin the whites of a number of eggs, carefully separating the germ, and all portions of yolk. To each ounce of this albumen add 1 drachm of distilled water, in which are dissolved 6 grains of iodide of potassium; also to every 5 ounces of the mixture add 1 drop of ammonia. Beat the whole to a stiff froth with a bunch of quills, and allow the liquid to settle till the following day.

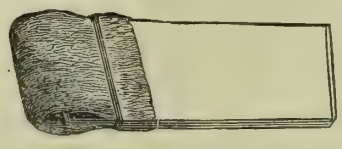
To Albumenize the Plate.—The glass plate must be cleaned very thoroughly, dried, and polished just before use. Attach to the under side of it a gutta-percha plateholder, having a wooden handle a foot long. Then breathe on the plate, and holding it horizontally in the left hand, pour upon the centre of it a sufficient quantity of the albumen from the basin to cover it, allowing the albumen to filter through an opening in the dry froth or crust. Make the albumen flow backwards and forwards over the plate three or four times, and then allow the excess to run off into a separate basin, from which it must be carefully filtered before being used a second time. In coating the plate, be careful to remove with the point of a fine camel-hair pencil any air-bubbles which may have formed upon it. Next, take the handle of the holder between both hands, and with the plate in a vertical position, spin it round quickly for a minute or so, in order to drive the albumen to the edges by centrifugal force. This done, remove the excess of albumen from the edges by means of a pipette, and dry the plate before a clear fire, keeping it rotating all the time by means of the handle, as before directed. When dry it is ready for the next operation. Albumenized plates may be put away in a plate-box, and kept in a dry place for a considerable time without deterioration. Care must be taken in the operation of albumenizing the plate that no particles of dust adhere to it.

A good plan of applying albumen and other like solutions is that adopted by Valentine Blanchard, who employs for the purpose what is termed the "Blanchard Brush." See Fig. 16. This is a strip of glass, 2 or 3 inches broad and 4 or 5 inches long; on one end is fastened a loop of swan's down calico, a

cotton material twilled on one side, and with a long plush-like nap on the other. The nap must be outwards; two thicknesses will be found better than one, and the loop can be readily fastened to the end of the glass by a small elastic band.

Solutions of any kind can be spread with the most perfect uniformity by the aid of this brush.

Fig. 16.



To Excite the Plate.—Place it on a dipper, and immerse it quickly and without hesitation in a vertical bath of aceto-nitrate of silver, made thus:—Distilled water 1 ounce, nitrate of silver 50 grains, glacial acetic acid 1 drachm. Leave it in the bath for a couple of minutes, then wash it well in clean water, and lastly in distilled water, and set it up to dry. When dry, put it away in the plate-box until ready for use in the camera. It may be preserved in a sensitive state for several days. Some persons add a few drops of a solution of potassium iodide to a new nitrate bath, and filter it on the following day, in order to saturate it with iodide of silver. When this is done, a new bath is not so liable to attack the iodide of silver in the film.

The Exposure.—Albumenized plates, from which the excess of free nitrate of silver has been removed by washing, are, whether used in a dry or wet state, extremely sensitive to light; but when only slightly washed, exposed at once, and developed with a strong developer, a much shorter exposure is sufficient.

To Develop the Image.—Immerse the plate in distilled water; then place it on a levelling-stand, and pour over it a saturated solution of gallic acid, to which a few drops of aceto-nitrate of silver have been added. The development occupies about twenty minutes.

To Fix the Picture.—Wash the plate in rain water, and pour over it a nearly-saturated solution of hypo-sulphite of soda. This will quickly remove the yellow iodide of silver from the film. Then wash the plate well under a tap, and dry it before the fire.

A great many modifications have been adopted with albumen to give greater sensitiveness and quickness of effect. Serum of milk, honey, and a dense solution of sugar have been mixed with the albumen, in order to get a coating of silver possessing more body than can be obtained by the albumen alone. Hunt introduced the use of potassium fluoride mixed with iodide; and this method, in the hands of M. Blanquart Everard, is said to be so sensitive as to give pictures on instantaneous exposure.

The Calotype or Paper Processes.—These processes are founded on the same principle as the collodion and albumen methods, the only difference being that the vehicle for supporting the chemicals is paper instead of a collodionized or albumenized plate. It is true that but little use is made of this branch of photography now-a-days, for paper negatives are seldom resorted to, except for enlargements; at the same time, calotype is too valuable a process to be ignored, for if paper negatives lack the transparency and sensitiveness of collodion films on glass, their supple character is a quality not to be despised.

Considerable attention must be paid to the quality of the paper. That most suitable is a white paper as free as possible from mineral matters, having a close fibre, sized either with starch or gum, and well pressed, to render the surface fine, even, and homogeneous throughout. Unsized paper absorbs too much of the materials, and the picture is developed rather in the body of the material than upon its surface.

The calotype processes may be classed under two heads. In the first the paper is coated with insensitive iodide of silver, and then excited by a weak solution of acidified gallo-nitrate of silver; in the second, the paper is first coated with an alkaline iodide, and then excited by immersion in a strong bath of nitrate of silver, the excess of free nitrate being subsequently removed by washing. In the processes of Class I. the paper is iodized with iodide of silver; in those of Class II. with a soluble alkaline iodide. The first kind of iodized paper may, for convenience, be called *argento-iodized* paper, the second kind simply *iodized* paper.

Class I.—There are *two* methods which come under this head. In the first, argento-iodized paper is prepared by what is called the *double wash;* in the second, by the *single wash.* In all other respects the two methods are identical.

To Argento-iodize the Paper by the Double Wash.—Float the face of the paper on a bath containing 20 grains of nitrate of silver to the ounce of distilled water. Let it remain a minute or two in the bath, then hang it up to dry. Next immerse it in a solution containing 25 grains of iodide of potassium to the ounce of distilled water. Let it remain a minute or two in this solution, the exact time depending on the kind of paper employed, and requiring to be ascertained by experiment. If too short a time is allowed, the whole of the nitrate of silver is not decomposed, and the paper darkens in the light; if, on the contrary, too long a time is allowed, the iodide of potassium in the bath dissolves the iodide of silver in the paper. The time of immersion in the iodide-bath is therefore rather critical. On removing the paper from the bath, let it drain, and then immerse it in a pan of water, in which it must be allowed to soak, the water being changed several times, until the *whole* of the free iodide of potassium is removed. This soaking operation is rather troublesome, and the texture of the paper is decidedly injured by it. Should any excess of iodide of potassium remain in any part of the paper, it would decompose the weak exciting solution and produce insensitive iodide of silver, and consequently a white patch in the negative. When the paper has been sufficiently washed, hang it up to dry. It is

of a yellow primrose colour. When dry, it may be kept for use in a portfolio. It is not sensitive to light.

To Argento-iodize the Paper by the Single Wash.—Lay the paper on a board with a piece of blotting paper under it, and brush over it a solution of silver iodide in potassium iodide, technically, "double iodide." The best kind of brush is V. BLANCHARD'S (described *ante*), or a large round one of camel's hair, bound with a string or silver wire. Apply the solution copiously both longitudinally and transversely, inclining the board, and keeping a flowing edge. Hang up the paper to dry in a room having a pure atmosphere. When very nearly or even quite dry, immerse the paper in a pan of water as before, to remove completely the excess of potassium iodide which it contains. Two or more papers should not be soaked in the same pan, but each paper ought to have a separate one. When sufficiently washed, an operation which requires several hours, dry, and keep for use.

The solution called "double iodide" is made by dissolving 20 grains of silver nitrate in 1 oz. of distilled water, and adding crystals of potassium iodide, a few at a time, until the yellow turbidity at first produced in the solution is quite cleared up. The quantity required is nearly half an ounce. The solution should then be filtered.

Argento-iodized paper will retain its good qualities for some weeks. Some persons even affirm that it may be kept for an indefinite period in a dry place. It is said to be improved by exposing it for an hour or two to strong sunshine. When this is done, it should not be excited immediately after insulation, but kept for some days previously in the dark, since it has been found that paper absorbs light in sufficient quantity to react on a sensitive surface placed in contact with it in the dark.

On comparing the two foregoing methods of iodizing the paper, it will be seen that the first is the most economical, but at the same time the least certain. A considerable quantity of potassium iodide is wasted in the second mode of iodizing, and the washing operation is rather more tedious.

To Excite the Paper.—Make a saturated solution of gallic acid in cold distilled water, which call solution A; and another, by dissolving 50 grains of silver nitrate in 1 oz. of distilled water, and adding 1 drachm of glacial acetic acid, which call solution B. Immediately before use, mix, in a chemically clean measure, 1 oz. of distilled water, 15 drops of solution B, and about as many drops of solution A, the number of the latter depending on the temperature and kind of paper employed.

Lay the paper on a board with a piece of blotting paper beneath, and apply the mixture copiously with a clean BLANCHARD'S brush. Hold up the paper to drain for a minute, then abstract the surface moisture with clean blotting paper, and place it in the dark slide.

The Exposure.—The average time of exposure, with a good light, a lens of 15 inches' focus, and a half inch stop, is seven minutes.

To Develop the Picture.—Lay it on a board, and brush over it, with a clean BLANCHARD'S brush, a mixture composed of 3 parts of solution A and 2 parts of solution B. The picture, the darker parts of which are at first faintly visible, soon comes out of a fiery red tint. At this stage of the development it is necessary to check it, in order to obtain dense blacks instead of feeble reds in the darker parts of the negative. To accomplish this, brush over the picture, and complete the development with a solution of gallic acid alone.

Under this treatment the reds soon darken and intensify, and become eventually opaque blacks. The active development should occupy about twenty minutes. It is an excellent plan, after having brushed on the gallic acid, to lay the paper face downwards on a horizontal glass slab, on which a quantity of gallic acid solution has been previously spread.

To Fix the Picture.—When the details are fully out, and the blacks of the proper intensity, wash the negative with water, and then immerse it in a solution containing 1 part of hyposulphite of soda (sodium thiosulphate) to 4 of water. Let it remain until the whole of the yellow silver iodide dissolves; then wash and soak in water for several hours, changing the water several times, in order to remove the whole of the hyposulphite from the paper, and hang it up to dry.

The negative is now finished, and may be waxed at any convenient time in order to render it more transparent. This is done by melting some white wax in a vessel placed in a shallow pan of boiling water, applying it with a clean hog's hair paint brush to the picture, which should be placed between sheets of blotting paper, and a moderately-hot iron passed over the whole until no shining patches of wax are seen.

There are one or two important points to be observed in this process. If the iodized paper is excited with a weak solution of aceto-nitrate of silver containing no admixture of gallic acid, it is quite as sensitive, or even *more* sensitive than before; but the negative is devoid of density, and the dark portions are grey, feeble, and metallic, like the dark parts of a collodion positive on glass when viewed by transmitted light. This shows that it is necessary to employ some such substance as gallic acid to continue, as it were, the chemical effect of the radiant light, or the proper tones cannot be produced. If, on the other hand, too much gallic acid is added to this solution, the reducing effect is so great that the paper becomes brown all over, particularly in hot weather. The process has therefore its drawbacks and uncertainties, particularly in that season of the year when photographic tourists are most in want of a good process. A good test of the proper state of the sensitive paper is to take a strip into the light. If it darkens instantly to a cold grey tint, incapable of being intensified by the further action of light, the negatives will probably be grey and feeble; but if it assumes a redder tint, which becomes still darker by continuing the exposure, there is sufficient matter present to give a good intense picture.

Calotype Processes—Class II.—In these processes the operations consist in first impregnating the paper with an alkaline iodide; next, rendering it sensitive by immersion in a strong bath of aceto-nitrate of silver, and developing with a weaker solution of gallo-nitrate of silver than that used in the foregoing process.

To Iodize the Paper.—Immerse a number of sheets, one by one, in a solution of potassium iodide containing 20 grains of the salt to the ounce of distilled water. Let them remain together in the bath for at least two hours, then hang up to dry.

To Excite the Paper.—Immerse it in a bath of aceto-nitrate of silver, containing 35 grains of nitrate of silver, and 2 scruples of glacial acetic acid to the ounce of water. First, float the face of the paper for a few seconds on the bath, then immerse it entirely for nearly three minutes, and then remove it into a dish of distilled water. Rinse well, then press it between blotting paper and put it into the slide, with its face to the front shutter.

The Exposure.—This is about the same as in the former process.

The Development.—The paper will scarcely exhibit any trace of an image. Immerse it in a solution of gallic acid, to which a few drops of aceto-nitrate have been added. The picture should be of a red tint (not grey), and should darken in the course of the development to an intense black in the deepest parts. The dish should be chemically clean, and the developer should remain colourless throughout; the whites of the picture will not then be discoloured, and the development will proceed much more quickly.

If the picture comes out grey and metallic, exhibiting all the detail, and having but little intensity, it indicates the want of a reducing agent in the sensitive film. To remedy this, add a little sodium citrate to the iodizing solution. This will entirely alter the character of the picture, increasing the density of the black, and also the necessary time of exposure. Sugar, honey, gelatine, and substances of this kind added in large quantity to the iodizing solution, produce little or no effect.

As a rule, it may be considered that organic salts, which both decompose silver nitrate and form insoluble silver compounds, act most powerfully in producing blacks; for instance, gallic acid, when added to silver nitrate, forms a mixture which is immediately decomposed by light, metallic silver being produced. It is a convenient plan, when travelling, to develop without a dish, by turning up the edges of the picture and making it into a tray, into which the developer may be poured and spread with a glass rod.

To Fix the Picture.—Proceed as in the former process.

Waxed-paper Process.—Wax is nearly inert as regards its power of combining with silver; its presence does not modify the character of the negative in any appreciable way as regards density. The only benefit derived from its introduction in the first stage of the process is, that it stiffens the paper, and renders it less liable to be torn. There is some difficulty in getting a sheet of waxed paper to imbibe the solutions. This may be overcome by dissolving a few shreds of gelatine in the iodizing solution, and by adding a little alcohol to the gallic acid. In all other respects the waxed-paper process is the same as that previously described.

The other processes of Class II. are merely modifications of the waxed-paper process in its simplest and best form, as described above. They consist in adding various organic substances, such as rice-water, gelatine, honey, and the like, and also bromides, cyanides, fluorides, &c., to the iodizing solution. Most of the organic substances are nearly, if not absolutely inert, and many of the mineral salts added are of very questionable utility. Potassium bromide may, however, be employed to replace the iodide with good effect, especially in taking landscape views, since it gives a better result as to light and shade. Cadmium iodide is also sometimes used instead of potassium iodide. The negative is free from the white spots which sometimes occur when a crystal of iodide of potassium remains undecomposed. But the cadmium nitrate introduced into the nitrate bath has an acid reaction, which renders the paper less sensitive, increases the difficulties of bringing out the details of the shadows, and diminishes the density of the blacks.

The Printing Processes.—There are several methods of printing positives from a negative. Some of these consist in producing prints upon paper, others in producing prints upon glass, ivory, fabrics, &c.

Printing on Albumenized Paper.—No one nowadays thinks of preparing his own albumenized paper, for it can be obtained in commerce of a far superior nature than it could be made by any one but a manufacturer. There is a great difference in the paper of various makers, and experience alone will prove which is best suited to the photographer's use. There are two distinct classes of paper in the market, termed *Rive* and *Saxe*, the former of which is generally employed where great brilliancy is desired, as in the case of small portraits and the like; for landscapes and larger portraits Saxe paper is usually preferred, as it has a more uniform appearance, and is not so liable to metallic spots and other defects as the Rive. In a highly albumenized paper, too, like the latter, the prints are apt to blister in the fixing bath, or in other words, water forces itself between the paper and the albumen film, often rendering the pictures useless. A good plan to avoid blistering is to employ two fixing baths, that in which the prints are introduced first being much weaker than the other. Schnauss says that damping the albumenized paper on the back, before it is sensitized, will also have the effect of preventing blisters.

The albumenized paper is sensitized by floating for two or three minutes upon a solution of nitrate of silver, 60 to 70 grains of the latter to the ounce of water. The solution becomes impoverished after several sheets have been sensitized, and then a fresh quantity of nitrate must be added. The strength of the solution should never be allowed to fall much

below 60 grains per ounce, if good and vigorous prints are desired. If the liquid becomes discoloured, it is shaken up with a little kaolin; and when this has subsided the clear solution is decanted off.

After sensitizing (in the dark room, of course), the sheets are hung up to dry on lines by means of American clips, and may then be put into the printing frames under a negative. Although there is no actual necessity for doing so, the pictures will be much brighter and fresher if the paper is sensitized, printed, toned, and fixed the same day. The printing is carried rather more deeply than the finished picture is required to be, for the impression loses some of its vigour subsequently in the toning and fixing baths. It should be borne in mind that unless the paper is pressed firmly against the negative film while in the printing frame, the impression will not be a sharp one. The prints are kept from the light until wanted for toning, and then are washed in two or three changes of water (which should not be thrown away, as they contain much silver), and then placed one by one in the toning bath. This is made up by preparing, in the first place, three separate solutions:—(1), 2 drachms of chloride of gold dissolved in 15 ozs. distilled water; (2), 1 oz. carbonate of lime mixed with 15 ozs. boiling water; (3), 1 oz. borax mixed with 15 ozs. boiling water. Of the gold solution half an ounce is taken, and of the other two 1 oz. each; and when mixed together the compound is allowed to stand for a couple of hours, and is then filtered for use. This amount will tone one sheet of paper. The liquid will keep any length of time, and is recruited from the stock bottles just as occasion requires. The toning bath recommended by HUGHES is made up a couple of days before use. It is thus composed—

Chloride of gold,	7½ grains.
Acetate of soda,	¼ oz.
Carbonate of soda,	¼ oz.
Distilled water,	40 ozs.

The prints are turned over and over in the toning solution until they have assumed the tint most agreeable to the photographer, who has only to bear in mind not to over tone. Wash the prints after they come out of the toning bath, and then place them for ten minutes or a quarter of an hour in the fixing bath, made up of—

Hyposulphite of soda,	1 oz.
Water,	8 ozs.

After fixing it is well to wash the prints in a moving stream of water for four and twenty hours; but if rinsed in alternate changes of warm and cold water, a much less period is sufficient.

Many substances have been proposed for admixture with the silver bath, as a means of preserving the paper in good condition for some time after it has been sensitized—such as sugar, citric acid, &c. Another plan of keeping sensitive paper white, after sensitizing, is to wash the surface as soon as it comes from the silver bath in a few changes of water. Washed paper, when dried and preserved well from the light, will keep many weeks in good condition; but before being placed in the printing frame, it must be subjected first of all to the action of ammonia fumes (in a box with a saucer of liquid ammonia), or the pad of the printing frame must be stuffed with powdered carbonate of ammonia.

Printing on Plain Paper.—A fine paper should be employed, such as *Saxe*, or other possessing a uniform surface; and this is floated upon a salting bath made up in the proportion of 1 oz. of distilled water to 4 grains of gelatine and 4 grains of common salt. When dry, the paper is treated as if it were albumenized, being sensitized, toned, and fixed in the usual manner.

One of the great causes of fading of albumenized prints is their defective washing, after they have been fixed in the hyposulphite of soda bath. Unless this body is perfectly removed by subsequent washing, albumenized pictures very soon become yellow and fade away. The sulphur in the hyposulphite is liable to form various compounds with the silver and albumen in the picture, and thus bring about changes which are injurious to the prints. Four and twenty hours is usually cited as the time for pictures to remain in flowing water to remove all traces of hyposulphite, and washing machines of various kinds have been invented for securing a thorough rinsing of the prints. One great thing to be attended to is not to allow the pictures to mass together in the washing trough; they should be put in singly, and if possible be prevented from clinging to each other. Automatic rocking troughs and siphon arrangements are employed to this end; for an entire change of the washing water should be made frequently, the prints being allowed to drain now and then before being put into a fresh supply of water. Varying the temperature of the changes of water, now using hot and now cold, is a good plan. There is, as SPILLER has shown, another danger of discoloration in albumenized prints; the silver forms with albumen albuminate of silver, which in the whites of the picture gradually becomes acted upon by light and darkens, thus degrading the high lights of the print. A plan has been brought forward by Dr. GAYER which, that gentleman states, produces permanent silver prints, and which mainly rests upon employing a maximum quantity of hyposulphite in the fixing bath, and operating in the dark. He recommends dissolving 1 oz. of hyposulphite of soda in 8 ozs. of water in a perfectly clean glass bath; having taken it into the dark room, immerse in it one print, not more than 8 inches square, for ten minutes, or at most a quarter of an hour. Then take the print out, and rinse it in two waters for a few minutes before removing it from the dark room; afterwards let it receive the usual washing in plenty of water, the latter operation being performed in the daylight. The hyposulphite solution is then thrown away, as it is quite useless for fixing a second picture. Dr. GAYER says that ten years' experience in India has shown him that prints treated in this way remain unaltered and fresh-looking, while those manipulated in the ordinary way have faded sooner

or later. The chemical explanation offered is as follows:—Chloride of silver, although perfectly insoluble in pure water, is easily soluble in a solution of hyposulphite of soda; but the hyposulphites of silver thus formed are extremely unstable. Chloride of silver forms two series of double salts with an alkaline hyposulphite, such as the hyposulphite of soda. Of these sodio-argentic hyposulphites, whose chemical symbols are $Ag_2Na_4S_6O_9,2H_2O$ and $AgNaS_2O_3,2H_2O$, the first easily dissolve in water, the second are nearly insoluble. All these double salts decompose very easily when heated and exposed to sunlight, yielding sulphite and sulphate of silver. They are also decomposed by alkalies and excess of the alkaline hyposulphites; and if to a solution of the soluble $Ag_2Na_4S_6O_9,2H_2O$ in hyposulphite of soda more silver salt is added, the insoluble sodio-argentic hyposulphite $AgNaS_2O_3,2H_2O$, is formed; and it is this latter highly unstable insoluble salt which, once formed in the photograph, cannot be washed out of it, and decomposing sooner or later, destroys the picture. The object of Dr. GAYER'S process is to prevent the formation of this insoluble salt in the print, and to prevent the decomposition of the soluble sodio-argentic hyposulphite while the photograph is in the hypo-solution. This can be done, he affirms, by keeping the proportion of chloride of silver very low in proportion to the quantity of hyposulphite of soda, and excluding the light while the process is being carried on. Captain ABNEY, R.E., with a view of making albumenized prints more stable, has made some experiments with albumen with a view of eliminating the sulphur contained, and thus securing a product which would be less open to objection. It is a moot question, however, whether sulphur is not a constituent of the albumen; and whether in separating it, either by chemical or mechanical means, the character of the albumen will not be altogether changed.

Hyposulphite of soda also exists frequently in white paper and cardboard. For this reason the photographer must choose carefully the mounts upon which the finished silver print is to be placed. The simplest test is with iodine, a piece of cardboard being soaked for some hours in water, and the liquid then tested for hyposulphite.

Uranium Printing.—In this process a sheet of paper is immersed in a saturated solution of nitrate of uranium, and dried in the dark. It is then exposed, under a negative, to sunshine for a few minutes. Where the light acts the uranic salt is reduced, and a faint positive picture obtained. This is intensified to a deep purple tint by immersing the paper in a solution of chloride of gold; strength, half a grain to the ounce of distilled water. After which it is well washed in water, dried, and the print is finished.

Printing by Development.—Immerse paper in a thin solution containing 6 grains of salt and 1 part of potassium iodide to the ounce of rain water. When dry, brush over it the following solution of nitrate of silver:—

Distilled water,	1 oz.
Nitrate of silver,	30 grains.
Lemon juice,	6 drops.

Expose in the pressure frame until a faint image is produced; this will require a few seconds only. Then turn up the edges of the paper; place it upon a sheet of glass, and pour into it saturated solution of gallic acid. When developed, wash in two or three changes of water, and fix it by the same treatment as that described in the ammonio-nitrate process; leaving out the gold toning as unnecessary.

Printing on Silk, Linen, and other Fabrics.—BADEN PRITCHARD gives the following advice regarding the production of silver photographs upon textile fabrics:—A densely woven material should be selected, and if cotton or linen is to be used, these must be obtained as free from dressing as possible; no glazed stuff of any description can be employed. The starch or stiffening is removed by allowing the fabric to remain for a quarter of an hour in warm water containing a small quantity of potash in solution, and afterwards rinsing it well in hot water. When dry, the fabric is stretched and mangled, to render it smooth, and albumenized with a mixture of—

Chloride of ammonia,	2 grams.
Water,	250 c.c.
White of two eggs.	

The ammonium salt is dissolved in the water and put into a large stoppered bottle, and the white of egg having been beaten to a froth, is added by degrees; the mixture being well shaken and allowed to subside after every addition of albumen. After standing twenty-four hours it is strained through a piece of muslin, and is ready for use. The surface of the fabric is allowed to remain in contact with the albumen for about five minutes. It is then dried slowly and passed through a rolling press, to give it a smooth surface; sometimes a second treatment of albumen is to be recommended. The silver bath should be rather strong, about 70 grains of silver to the ounce of water. The fabric is floated for five or six minutes, and when dry is easily manipulated in the printing frame. It must be rather overprinted, as it loses much in toning, and it should be toned and fixed as soon as possible; the whites of the picture are not fully restored till the print has been fixed. The operations of sensitizing, printing, toning, and fixing should be all carried out in one day. The negatives for this kind of work must be brilliant and vigorous; a soft delicate negative, which gives the best results on paper, is not so well suited for the purpose.

Any stains which may have been formed on the fabric during the process, are best removed by brushing over with a solution of iodine, and washing out with hyposulphite of soda, care being taken not to touch the border of the picture with the iodine. The solution of iodine is prepared by adding three parts of iodide of potassium to one part of iodine, and dissolving the same in ten times their bulk of water.

Collodio-chloride Printing.—This process is the invention of Wharton Simpson. To prepare the collodio-chloride, a good normal collodion should be used, rather thick, giving a film not too horny or brilliant, and perfectly transparent. In regard to the salts, chlorides of various kinds may be used, those of strontium, calcium, and lithium being all suitable. There must not be too much nitrate of silver added to the collodion, otherwise crystals will be formed on the drying of the film; too small a dose of silver, on the other hand, causes a lack of vigour. The collodio-chloride is prepared thus:—Some nitrate of silver is dissolved in methylated spirit—as much as 16 grains of the salt to the ounce of spirit being dissolved readily if triturated in a mortar; the spirit added gradually until all is dissolved. To 1 oz. of this spirit is added 1 oz. of ether and the requisite amount of gun-cotton (say 6 to 10 grains to every ounce of ether and alcohol); and afterwards there is added three-quarters of a drachm of solution of chloride in alcohol, containing 16 grains to the ounce. This is added a few drops at a time, the collodion being shaken between each addition. In a few minutes the decomposition is complete, and something like an emulsion is formed, with excess of about 3 grains of nitrate of silver in each ounce. This is immediately ready for use, and may be kept, screened from the light, for a period at any rate of many months. Another mode of preparation is to produce three solutions as follows:—

No. 1.	Nitrate of silver,	1 drachm.
	Distilled water,	1 "
No. 2.	Chloride of strontium,	64 grains.
	Alcohol,	2 ozs.
No. 3.	Citric acid,	64 grains.
	Alcohol,	2 ozs.

To every 2 ozs. of plain collodion add 30 drops of No. 1 solution, previously mixed with 1 drachm of alcohol; then 1 drachm of No. 2 solution gradually, shaking well at the same time; lastly, half a drachm of No. 3 solution. In a quarter of an hour the collodio-chloride will be fit for use.

This collodio-chloride may be applied to any basis desired—paper, porcelain, opal glass, ivory, &c. When applied to paper which has not a very uniform and polished surface, there is a tendency in the film to peel off; although by careful manipulation of the finished prints, not allowing them to become too dry before mounting, this inconvenience is obviated to a great degree. The collodio-chloride is applied to these surfaces in the same way as ordinary collodion, being poured upon the paper or glass and dried. A sizing of arrowroot or gum tragacanth should be first applied to the paper, to render it non-absorbent; the sheet is turned up at the sides to form a tray, fixed upon a flat board with pins, and then coated with the collodion. It should dry very thoroughly before being placed in contact with the negative. Collodion paper thus prepared should be printed rather more deeply than albumenized paper; and if sufficient vigour cannot otherwise be obtained, the sensitive surface is formed with ammonia vapour for a short time before it is put into the printing frame. Any toning bath may be employed, but an old dilute acetate bath answers best. A bath of hyposulphite of soda and gold also answers well. The fixing is done in a hyposulphite of soda solution—3 ozs. to a pint of water. Five minutes' immersion is generally sufficient. The prints must be thoroughly washed afterwards, but do not require such continued immersion in water as albumen photographs. The pictures should not be deeper than a warm brown or purple, as they lose no depth in the hyposulphite bath, and are blacker after drying. Glass plates should have a preliminary coating of dilute albumen (the white of one egg in 8 ozs. of water) before receiving the collodio-chloride; and after the latter is dry, it is formed with ammonia, the plate being simply held over the mouth of a bottle of strong liquid ammonia, and moved about until the whole surface is brought in contact with the fumes. When completely formed, the bright surface becomes dulled. An intensifying solution may be used after printing, if increased vigour is required. The solution is prepared as follows:—

Gallic acid,	75 grains.
Acetate of lead,	50 "
Acetic acid,	2 drachms.
Distilled water,	26 ozs.

The solution should be filtered, and a few drops of a 20-grain nitrate of silver solution added just before use. The solution is applied to the plate in the dark room, just as in the wet collodion process. The image will be seen gradually to acquire intensity, but it must be borne in mind that the print when dry is much more vigorous than when wet. The picture is washed, toned if necessary, and fixed.

A good plan of reproducing photographs from a transparent positive is this:—A picture on paper is waxed to render it transparent, and then used for printing from. A well cleaned glass plate is coated with collodio-chloride, as described above, and upon this a print is obtained from the transparent positive. No toning is required in this case, but a little intensifying; and the result is a collodio-chloride *negative*, possessing all the detail and qualities of the original positive print in a most perfect degree.

Pigment or Carbon Printing.—Printing in permanent pigments, or in carbon, as it is often called, is based, like most of the recent printing processes, upon the action of light upon the bichromate of ammonia and potash, when mixed with certain organic substances. Gelatine, isinglass, gum, and similar substances, if mixed with a small percentage of the bichromates above alluded to, and exposed to the light for a short time, become insoluble, and refuse to dissolve either in warm or cold water. This fact Mungo Ponton first observed in 1839, that gentleman describing a process of photographic printing by means of bichromate of potash in the same year. The method consists in taking an ordinary sheet of sized paper (faced with gelatine therefore), dipping it into a solution of bichromate of potash, and after drying it in the dark, printing upon it in the sun the image of any object placed thereon. By subse-

quently washing the sheet in water, and in this way removing those portions of the salt which are still soluble (and which have been protected from sunlight), a brownish picture is obtained that may be regarded as perfectly permanent.

Poitevin appears to have been the first to elaborate a pigment or carbon process—or, in other words, to obtain photographic impressions formed of some permanent colouring matter; and this was effected by adding to the mixture of bichromate and gelatine a third body, in the form of powdered vegetable charcoal, Indian ink, or some such material. This was in 1855. The inventor prepared a mixture of the three ingredients we have mentioned, and spread it upon paper. The sheet thus faced with a black compound was, after drying, put under a negative, and printed in sunlight for a sufficient period. When taken from the printing frames, portions of this surface had, of course, been rendered insoluble —those parts, to wit, where the negative had allowed the light to pass through and attack the film; and these insoluble portions, when the sheet was subsequently washed in warm water, refused to leave the paper, and formed an image corresponding to that upon the negative. The bichromate mixture, where it became insoluble, kept the pigment imprisoned, and the colouring matter thus fixed formed the photograph. The print produced in this way was not very delicate, but still it was a carbon photograph, and as such was comparatively imperishable; for the picture being made up simply of minute particles of insoluble pigment, was not so liable to perish as those produced in the chloride of silver printing process by the reduction of a metal salt. Other inventors quickly followed M. Poitevin, but none of them were more successful than the French inventor.

It was not, indeed, until the Abbé Laborde in France, and independently of each other, Burnett, Swan, and Blair in Great Britain, added an improvement to the process, that carbon printing was capable of furnishing pictures possessed of delicate half tone. Carbon photographs had a want of depth, and were bereft of all delicacy before these gentlemen suggested a sensible modification in the process. This was to develop the film or cake of bichromated gelatine from the *back*, instead of from the front, after it had been printed under a negative. Blair's method was to coat transparent waxed paper with the sensitive mixture, and to allow the light from the negative to traverse the waxed paper (the negative being laid next the paper), and thus impress the pigment on the inside; then by dissolving away from the surface of the pigment he obtained an image with good half tones, but which, owing to the opaqueness of the waxed paper, was defective in the whites. A French experimenter, M. Fargier, succeeded better; he coated a glass plate with the sensitized pigment and exposed the same to light, the pigment surface next the negative. When the pigment surface had been sufficiently exposed he coated the same with collodion, and when the film had dried, placed the whole in a vessel of warm water. All the pigment mixture that was still soluble was speedily removed, and then remained an image in carbon, adhering to the film of collodion. In this case the image was of a most perfect character; for being washed from the back (the film of collodion still adhered to the face), the most delicate half tones were obtained. M. Fargier's method was in truth the first perfect plan suggested, and it is, with slight modification, the one in use at the present day. In 1864 J. W. Swan patented a process, which was of an eminently practical nature, and was in fact instrumental in causing photography in pigments to be taken up in an extensive manner both in England and abroad. Swan specified certain improvements in the making up of the sensitized pigment mixture; but the main point of the process was his method of developing and redressing the prints. Paper coated with a layer of the sensitive mixture, and termed *carbon tissue*, was printed against a negative in the ordinary way, the pigmented surface next the *cliché;* and after printing, a sheet of india-rubber paper was placed face downwards upon the tissue, and cemented together with india-rubber cement. The tissue was then plunged into warm water, which as a matter of course dissolved away all that was still soluble, leaving an image in carbon upon an india-rubber surface. The picture was now developed, but it was reversed, and required to be redressed before it could be seen properly. To do this a sheet of white paper was coated with warm gelatine, pressed down upon the image, and allowed to dry; and then by softening the back of the india-rubber paper with benzol this became easy to remove, and the image remained attached to the gelatine paper, and could then be seen in its proper aspect. Thus, to summarize the process, the picture was printed on the face of the tissue; this was then attached to the rubber paper while the development from the back went on; and finally the print was put back again to its original position upon a sheet of gelatined paper. This process of Swan's solved the problem of carbon printing as a practical method, and proved, moreover, a commercial success.

Of late, however, pigment printing has been further simplified by J. R. Johnson, who altogether obviates the use of india-rubber paper for cementing the exposed carbon tissue to during development. Johnson's process is generally termed the autotype method, to distinguish it from other plans of carbon printing. Paper faced with a mixture of bichromate, gelatine, and pigment, or as we have termed it, carbon tissue, is printed under a negative in the ordinary way, the pigment film next the *cliché*. When removed from the printing frame the sheet is put into cold water, which gradually permeates the gelatinous film and makes it swell; in a minute or two the tissue is removed from the water bath, and pressed face downwards upon a polished plate of glass or metal. To this impermeable surface the carbon tissue tenaciously adheres, in the same way exactly as a boy's leather sucker will adhere to a paving stone. A few minutes are allowed to elapse, and then the plate with the tissue sticking to it is

put into a warm-water bath of about 90° Fahrenheit. The paper backing is at once removed by the warm water (for it must be borne in mind that the tissue is face downwards), and there remains the film of black pigment adhering of itself to the surface of the plate. This is washed, and gradually dissolves away, leaving the photographic impression sticking to the plate. The picture cannot be removed by the warm water, for it consists of insoluble matter; and when it has been thoroughly washed and freed from the soluble pigment clinging to it, the photograph is dipped into cold water to stop any further action; and furthermore, into a strong solution of alum, which has the effect of tanning or fixing the gelatinous print. The latter is subsequently thoroughly washed and allowed to dry. We have now a perfect photograph before us upon a glass or metal plate, only it is reversed; so a sheet of white paper well sized with gelatine is put into hot water, together with the plate with the photograph, and the sticky surface of the paper pressed in contact with the image. On drying the sheet of paper spontaneously leaves the plate, bringing with it, attached to its surface by the gelatine, the pigment impression; and thus we obtain an impression in carbon not reversed, but in its proper aspect.

The above is termed the autotype double-transfer process, and is that generally used, as it is suited for all ordinary negatives. There is, however, a single-transfer process which yields prints of rather more delicate nature, only in this case the negatives used must be reversed. In the single-transfer process the carbon tissue is printed as before under a negative, and is then, after immersion in cold water to swell, placed face downwards upon white paper, and developed upon the latter, which forms, indeed, the ultimate support of the picture; for this does not require to be transferred again, if the negative from which it was printed was taken reversed.

Pigment pictures can be produced of any desired tint, for it is only necessary to change the colouring matter used when preparing the tissue.

Of the difficulties inherent to carbon printing, that of timing the exposure is perhaps the greatest. In silver printing we have a white surface, which gradually darkens; but in the present instance the sensitive surface is dark to begin with, and no apparent change takes place by the action of the sun. A photometer of some kind is usually employed, and the simpler it is the better. The most practicable is that employed by the Autotype Company, consisting of a little square wooden box, having a slit in the lid. A roll of paper tape, sensitive to light, is contained in this box, a small portion of it being visible through the slit in the lid; and every time the light blackens the tiny portion of paper exposed, and renders it of a colour similar to that of which the lid of the box is painted, the photometer has marked one degree. The sensitive tape is then moved forward, and a fresh portion of it submitted to the action of the light. Very thin negatives take one or two degrees to print—that is to say, the tissue requires to be left under them, exposed to the action of daylight, for the space of time required to blacken sensitive paper once or twice over; but negatives of ordinary density require four, six, and eight degrees. The density of a negative can only be judged by experience.

Pigmented paper or tissue can be purchased either sensitive (containing bichromate) or insensitive, in which latter case it is floated in the dark upon a 3 or 5 per cent. bichromate of potash solution, and dried. Sensitive tissue will keep good several weeks, if stored carefully away from the light. Some care is necessary in its development in warm water. Over-exposed prints may be developed, if necessary, in water a little above 90° Fahr.; but, as a rule, this temperature should not be exceeded. Insolubility of the tissue sometimes occurs when the same has become stale, but this is a defect not difficult to guard against. The surface of the picture may be varied at will, according to the nature of the plate upon which the development takes place. As the pigment tissue during development adheres very closely to the impermeable surface to which it clings, the image naturally enough adopts in some measure the character of the support. Thus a glass plate, having over it a film of collodion, will, if used as a developing basis, yield a print having a most glaring and brilliant surface; while a zinc plate, roughly grained, gives a heavy, dull print. A very suitable developing basis is that afforded by a polished zinc plate; for the latter imparts a finished appearance to the photograph and perfect transparency in the shadow, without, at the same time, rendering the surface too glaring or brilliant. Unfortunately in most cases a white developing surface is necessary, in order that the operator may see how far to push matters; for the grey colour of the zinc is rather misleading. Matt opal glass or biscuit porcelain are both suitable for the purpose, but they are rather costly, and, moreover, easily broken.

Photo-lithography and Photo-zincography.—Many excellent plans have been proposed for placing the photographic image upon stone and zinc, and printing from the same by lithography. No half tone can be obtained in this way in any degree of perfection; but in the reproduction of drawings, designs, line engravings, MSS., and the like, the processes are very successful. One of the methods in general use is that of Sir Henry James, which is employed at the Ordnance Survey Office, Southampton; but lately many improvements have been made in this kind of printing. Butter's process, as practised by that gentleman in the Royal Carriage Department at Woolwich, is a most perfect one; and being to our knowledge of an exceedingly practical nature, we give the details *in extenso*.

The Drawing or Design to be copied for reproduction should have well-defined black lines, and should not be shaded with Indian ink, or tinted with flat washes of any kind. It should be properly stretched on a level board, or pinned out as flat as possible, in order that all the lines may be kept in the same plane.

In Taking the Negative, select a situation where

diffused light falls upon the drawing; as when the lighting proceeds strongly from one direction, the grain on the surface of the paper and the glazed ink lines give false lights and shadows in the negative, causing some of the lines and figures to be broken and confused. The size of the intended copy being determined, it is marked on the ground glass of the camera, and the drawing placed in such a position as to reflect an image which exactly fills the space marked on the ground glass; the right angles at the corners being accurately preserved, which can only be done by keeping the plane of the picture or drawing parallel to that of the ground glass, and the centre in a line with the axis of the lens. Small stops are used to get sharp definition, and some point midway between the centre and outside parts of the drawing is used to focus by. The *collodion* must not be newly mixed, should be perfectly clear, and adhere well to the glass plate.

The Nitrate of Silver Bath is of the ordinary strength, but made slightly acid, to prevent any chance of fogging. The exposure in the camera should be sufficiently prolonged to get a fair deposit of silver, but should not be carried so far as to risk filling up the lines whilst developing; as one of the most essential conditions to insure success in the subsequent operations is to secure in the negative perfect transparency in lines representing the drawing, and as much opacity as possible in every other part.

The Developing Process which gives the best results is the following:—Develop in the first place by means of a 15-grain solution of sulphate of iron, with 15 minims of acetic acid, and stop the action the moment the lines are distinctly visible. After well washing the plate, if it appears very weak, pour over it a mixture of equal parts of the following:—

Pyrogallic acid,	8 grains.
Citric acid,	25 "
Distilled water,	2 ozs.
Nitrate of silver,	10 grains.
Distilled water,	2 ozs.

This should not be used unless the deposit is very feeble, and must be washed off before becoming much discoloured. The negative should now be fixed with a saturated solution of hyposulphite of soda, and the film rendered dense and opaque by first repeating the use of the mixed pyrogallic acid and nitrate of silver solutions; and after washing, pouring over the plate a saturated solution of bichloride of mercury until it has whitened; washing, and finally darkening with a weak solution of hyposulphite of soda (about 1 part saturated solution and 12 parts water). Before using the bichloride of mercury, the plate may be dried and the edges varnished, to prevent the collodion rising; and if a single application is not sufficient to obtain the requisite density, the treatment with mercury and hyposulphite of soda solution may be repeated. Great care must be taken in well washing the film after the use of the latter, since there is otherwise a liability to the formation of red and brown stains, which would render the negative altogether useless.

The Photo-lithographic Paper is prepared by dissolving separately 3 ozs. of the best gelatine ("NELSON'S opaque" answers very well) in 40 ozs. of hot water, and 2 ozs. of bichromate of potash in 10 ozs. of hot water; the two solutions are mixed together, and should then be kept from the light. When required for use the beaker, or other vessel containing the mixture, should be immersed in hot water for the purpose of liquefying the gelatine, which may then be poured into a flat porcelain dish, placed within another containing hot water; and the paper is then floated in the liquid for about seven or eight minutes, the corners being lifted and all air-bubbles carefully dispersed, so as to insure a perfect coating The sheet is then raised, drained over the dish, and hung up to dry, after which the process is repeated. Bank post paper is found to be most suitable, and before its preparation one side should be marked, so as to readily distinguish the prepared surface. The whole of this operation must, of course, be conducted in the dark.

When perfectly dried after the second coating, the prepared paper should be laid face downwards on a polished lithographic stone, heated and passed through the press in order to give it a smooth uniform surface; care being taken that no light gets to it, to insure which in this, as in subsequent operations, the lithographic press should be in the dark room, or used at night, or the stone may be lifted from the press and taken into the dark room each time it is necessary to handle the paper on it, using several folds of yellow paper as backing sheets, to protect the prepared paper during the transit.

The operation of printing is precisely the same as with albumenized paper, extra care being, however, needed that no light reaches the print. As the printed parts are of a yellowish-brown colour, while the whole surface of the paper is of a deep yellow, the difference between the two is scarcely discernible in the yellow light of the dark room; but the operator must not be tempted to examine the progress in daylight. It is also of the utmost importance that the image should not be overprinted, for if the action of the light extends to the general surface of the paper, it is altogether impossible to succeed in clearing the print in the next process; if, on the other hand, the image be underprinted, there is a great probability of the finest lines being rubbed away.

Inking the Impression is the next stage in the process after exposure, and again brings the lithographic press into requisition. The greasy ink used may be either the common litho-retransfer ink, with which the most satisfactory results have been obtained, or the following:—Grind together 2 lbs. of chalk lithographic ink and 1 lb. of middle linseed varnish; melt in an iron ladle 4 ozs. of Burgundy pitch, and add gradually 2 ozs. of palm oil and 2 ozs. of white wax; stir the mixture till it burns; and then put in the ink and varnish in small quantities at a time, stirring the whole well together. When required for use a small portion is melted with sufficient spirits of turpentine, so as to give it, when cold, the consistence of treacle. To ink the print, a polished lithographic

stone (having been cleaned with spirit of turpentine, if it has been used for the same purpose before) is charged with a very thin coating of the ink by means of a litho-roller, and the print laid face downwards upon it and passed through the press, using a rather lighter pressure than in ordinary printing. On taking up the print it should be found uniformly covered with a thin tint of the black ink: the thinner the layer of the ink, the sharper and finer will the drawing come out.

Removing the superfluous ink is accomplished in the following manner:—Prepare some strong gum water and warm it slightly; pour some hot water (about 100° Fahr.) into a flat porcelain dish, and upon it float the inked print, face upwards, allowing it to remain until the warm moisture has penetrated the gelatinous film, which will be known by the appearance of innumerable glossy patches over the surface of ink. Then pour off the water, leaving the print evenly spread on the bottom of the warm dish, and wash it very carefully with a soft sponge and the warm gum water. If the gelatine is of good quality, the negative sufficiently opaque, and no light has been permitted to reach the print beyond that which passed through the transparent parts of the negative, the coating of gelatine, and with it the greasy ink on its surface, will be removed from the paper with the slightest touch of the sponge, leaving behind such portions of the composition only as have been made insoluble by the action of light, and which consequently also retain the ink on them; gum water being incapable of attacking the grease and removing it from the paper, unless it can do so by first dissolving away the foundation of gelatine upon which it rests.

When all the superfluous ink has been removed, the print is washed in several changes of tepid water (not so warm as before), and hung up to dry. A careful examination will now point out any errors in the foregoing process. If the fine lines which lie close together, or the angles formed by the junction or crossing of the lines, are filled in with ink, and the drawing generally appears rough and wanting in sharpness, there has been too much ink on the stone in the inking process; if, on the other hand, the lines are very sharp and fine, but extremely pale and wanting in sufficient body to transfer themselves to stone, there has been too little (a very rare fault). If the ink leaves the paper sluggishly, and there remains behind a dark scum in patches over the drawing, light has affected the paper, either through the negative being not sufficiently dense (a very likely cause), or from carelessness in conducting the operations. If the lines are broken, and exhibit a tendency to leave the paper, the print has been under-exposed; whilst if the thick lines, dots, &c., are firm, sharp, and well defined, and the fine ones rotten and feeble, the negative itself is at fault, having its fine lines partly covered up in the intensifying process. This fault is not so easily discerned on looking through the negative as might be imagined, on account of the filling up frequently consisting of a thin yellowish veil, transparent to the eye and chemically opaque—a fault generally due to over-exposure and carrying the development too far previously to fixing, but occasionally due to insufficiently washing away the hyposulphite of soda in each operation in which it has been used.

The Transferring to Stone is performed in the same manner as with ordinary transfer in lithography.

M. RODRIQUES, a professor of chemistry at Lisbon, has also elaborated a process of photo-zincography, which is used with great success in the Government Topographical Department of Portugal. The details of his method are as follows:—

Preparation of the Negatives.—The ordinary phootgraphic processes are used, choice being made of that one which gives the most opaque density of ground and the greatest transparency in the lines.

Preparation of the Zinc Plates.—Very thin plates of metal are used, having a very even surface, which is polished with emery powder. Upon the plate, after it has been thoroughly cleansed from every impurity, is applied a very thin coating of the under-mentioned solution:—

Gelatine,	2 grams.
Bichromate of ammonia,	1 gram.
Water,	100 grams.

After drying over a gas flame the plate is exposed to diffused light under a *cliché*, in an ordinary printing frame, for a period varying from fifty seconds to a minute and a half, according to the opacity of the blacks (the blacks must be quite opaque). It is then allowed to remain for about five minutes, to allow the chemical action to proceed. After this the plate is covered with a mixture composed of ordinary lithographic ink and transfer ink, in the proportion of 4 parts of the former to 1 of the latter—the roller used for the purpose being one of very supple leather; and the plate is then plunged into cold water for three or four hours. It is needless to say that the last operations are conducted in the dark. The plate is next taken out of the water, and with the same roller the image is developed by depriving the plate of all the superfluous ink. The impression is put into tepid water for a period sufficient to dissolve away completely the parts where the light has not acted; the plate is further washed with cold water, drained, and as soon as dry covered with a solution of—

Water,	1000 grams.
Gum arabic,	40 "
Sulphate of copper,	2 "
Gallic acid,	5 "
Nitric acid,	½ gram.

Printing.—A printing press may be employed instead of a lithographic one. Every plate will yield from 200 to 300 impressions, and the same zinc plate will serve the purpose several times if properly cleaned with dry emery powder. By employing thicker plates, and etching the metal as in chemical engraving, sufficient relief is obtained for typographic printing. The main points of advantage in the process are—(1), that no transfer is necessary; (2), the printing is very rapid; (3), perfect

contact between the *cliché* and the zinc is insured during exposure to light; (4), no graining of the plates is necessary; and (5), there is great adherence of the sensitive film to the zinc, the former being exceedingly thin, and well cemented to the metal.

Another efficient process of photo-lithography, or Papyrography, as its inventor, Captain Abney, R.E., terms it, consists in taking a sheet of paper of suitable size, and coating it with a sensitive film, by floating upon a solution made up of—

Gelatine,	3 ozs.
Bichromate of potash,	1½ oz.
Water,	50 ozs.

When dry the operation is repeated, and the sheet hung up the reverse end. To give a fine surface to the paper, a preliminary coating of gelatine and alum may be applied. When perfectly dry the sensitive paper is put under a negative to print; and after removal from the pressure frame, it is put into cold water containing a little alum. After remaining immersed for some time to allow the soluble bichromate to dissolve out, the paper is put upon a flat support of glass, zinc, or any other firm basis, and the superfluous moisture removed by means of bibulous paper. Lithographic transfer ink is then applied by means of a soft leather roller, and the impression is then treated like an ordinary transfer, and put down upon a stone or zinc surface in the lithographic press. If the negative employed is a thin one, and causes what should be unaltered gelatine to be altered by the light, a stiff ink must be used, as an ink of this kind has a less degree of affinity for the parts which have been feebly acted upon. After the inking of the impression has been effected, it is sometimes advisable to reimmerse the print in a solution of alum. It is also advisable to dry the picture at this stage, and in the event of the whole of the bichromate not having been washed out, to expose it to light again, so as to insure the surface becoming as hard as possible, and thus preventing it from adhering to the stone or zinc when the image is being transferred. The impression should be damped before transfer.

Photographic Engraving.—This process was patented by Fox Talbot in April, 1858; it consists in etching, by chemical means, a positive photograph printed upon a copper plate.

Plates of steel, copper, or zinc, such as are commonly used by engravers, are employed. Before using a plate its surface should be well cleaned. It should then be rubbed with a linen cloth dipped in a mixture of caustic soda and whiting, in order to remove any remaining trace of greasiness. The plate is then to be rubbed dry with another linen cloth. This process is then to be repeated, after which the plate is in general sufficiently clean.

The sensitive coating for receiving the image is prepared by adding to about a quarter of an oz. of gelatine, dissolved in 8 or 10 ozs. of water by the aid of heat, 1 oz., by measure, of a saturated solution of potassium bichromate in water, and straining the mixture through a linen cloth. The best sort of gelatine for the purpose is that used by cooks and confectioners. Isinglass does not answer so well, since it sometimes has an acidity which corrodes the metal plates. In this case ammonia should be added to the mixture. The mixture of gelatine and potassium bichromate keeps good for several months. It remains liquid and ready for use during the summer months, but in cold weather becomes a jelly, and has to be warmed before employing it. It should be kept in a cupboard or dark place. The proportions given above may be considerably varied without injuring the result. The engraving process should be carried on in a partially darkened room.

A little of the prepared gelatine is poured on the plate to be engraved, which is then held vertically, and the superfluous liquid drained off at one of the corners. It is then held in a horizontal position over a spirit lamp, which soon dries the gelatine, which is left as a thin film of a pale yellow colour, covering the metallic surface, and generally bordered with several narrow bands of prismatic colours. These tints enable the operator to judge of the thickness of the film. When it is very thin, prismatic colours are seen over the whole surface of the plate.

The object to be engraved is laid on the metal plate, and screwed down upon it in a photographic copying frame. The plate is then placed in the light for a space of time varying from one to several minutes, according to circumstances. When the frame is withdrawn from the light, and the object removed from the plate, a faint image is seen upon it, the gelatine having turned brown wherever the light has acted. Finely-powdered gum copal or common resin is then spread over the surface of the plate, carefully and very evenly; care being taken to guard against putting on too much of the powder. The plate is then held over a spirit lamp, in order to melt the gum. This requires a considerable heat. The melting of the copal is known by its change of colour. The plate should then be withdrawn from the lamp, and suffered to cool. The gelatine being thus covered with a layer of copal; ferric chloride, the etching liquid, is poured on. This is prepared by dissolving hot ferric oxide in hydrochloric acid. After straining the solution to remove impurities, it is evaporated, and is then poured off into bottles. As it cools, it solidifies into a brown semi-crystalline mass, which when laid upon a surface of iron, copper, or zinc, attacks these bodies, being itself reduced to the state of ferrous chloride.

A bottle (No. 1) is filled with a saturated solution of ferric chloride in water; a bottle (No. 2) with a mixture consisting of 5 or 6 parts of the saturated solution and 1 part of water; and a bottle (No. 3) with a weaker liquid, consisting of equal parts of water and of the saturated solution. Before employing these solutions to etch the photoglyphic plate, the operator tests their power, by applying a portion of No. 2 bottle to metallic surfaces prepared as directed; and when the etching goes on too rapidly, adds to it a quantity of the saturated liquid in No. 1 bottle. On the contrary, if the

etching does not commence for a few minutes, or proceeds only slowly, it is a sign that the liquid is too dense, and requires dilution either with water or the contents of the third bottle; either of which ought, however, to be added very sparingly, as a small proportion of either gives great activity to the etching liquid. After the strength and power of the solution have been determined by three or four such trials, it may be poured on the prepared plate, and spread evenly with a camel-hair brush. The liquid penetrates the gelatin wherever the light has not acted on it, but does not penetrate those parts upon which the light has sufficiently acted. In this way the etching proceeds till all the details of the picture have become visible, which generally occurs in two or three minutes; the operator stirring the liquid all the time with a camel-hair brush, and thus slightly rubbing the surface of the gelatin. When it seems likely that the etching will improve no further, it must be stopped. This is done by wiping off the liquid with cotton wool, and then rapidly pouring a stream of cold water over the plate, which carries off all the remainder of it. The plate is then wiped with a clean linen cloth, and rubbed with soft whiting and water to remove the gelatine. The etching is then found to be completed.

Photo-galvanography.—This process consists in obtaining from a photograph, and by means of electro-plating, a metal plate in raised and sunk parts, from which impressions can be printed in printers' ink.

The positive print—generally on paper—is laid, face upwards, on a sheet of glass coated with gelatine, containing potassium bichromate and dried; it is then exposed to light in a pressure frame for a few hours. The picture on the gelatine is developed in raised and sunk parts by immersion in water. Where the light has not acted the gelatine swells; but where it has acted, the gelatine is hardened and does not swell. The picture thus formed is very curious, and resembles a positive by reflected light; the shadows and dark parts being rough, and the lights smooth and polished.

A mould of the picture is then taken in gutta-percha about half an inch thick, and a copperplate is made from the gutta-percha mould by electrolysis. The copperplate thus obtained is called the matrix. It precisely resembles the original gelatine picture. The plate from which the proof is to be printed is obtained from the matrix by the electrotype process. From the final plate, four or five hundred good impressions may be struck in the ordinary way. A considerable number of plates may be obtained from the matrix; also of matrices from the gutta-percha mould, and of gutta-percha moulds from the gelatine picture.

WOODBURYTYPE.—This process, the invention of WALTER B. WOODBURY, is perhaps the most perfect photo-mechanical printing process at present known. Although patented some time previously, it was in 1866 that the inventor published the first example of the process, by way of illustration, in the *Photographic News*, when the sterling value of the invention was at once apparent. Of late years several very material improvements have been made in the process by WOODBURY and others, and large establishments for printing by the Woodburytype or photo-relief process exist in London as well as in the large cities of Europe and America. The way in which the printing block is obtained and the mode of printing, are easily explained, the key-stone of the whole process being the power of light to render insoluble a mixture of bichromate and gelatine, when the latter is exposed to its action for a sufficient period —(See section on PIGMENT OR CARBON PRINTING).

The first thing to be done is to obtain the printing block. A negative of any description is taken and put into a printing frame with a film of gelatine, sensitized with bichromate. A good method of preparing this film is to coat a glass with collodion, and when this has set, to pour thereon a warm and thick solution of gelatine containing 3 to 5 per cent. of bichromate of potash. The film must be of tolerable thickness, and therefore two or more applications of the gelatine are usually necessary. When dry, this sensitive film is placed under the negative to be printed, the printing frame being placed at the bottom of a box, so that the rays can only come direct from above, and not from all sides. This is a very necessary precaution, because the printing goes to some depth into the gelatine; and if the light rays were not perfectly vertical, the impression would not be a sharp one. After printing, the film is put into warm water, or has warm water poured upon it, and this has the effect of dissolving out such parts of the film as may still be soluble. Where the light has been altogether screened from the film by an opaque part of the negative, there the gelatine is still quite soluble, and consequently the warm water produces quite a deep hollow in those parts; where the gelatine has been only partly shielded from the light by a slight covering of the negative—in the half tones, for instance—there the warm water has but little action, but, nevertheless, washes away the gelatine in a slight degree; while under the transparent parts of the negative, where the light has had free access to the film, there the gelatine is perfectly insoluble, and consequently no amount of washing will remove it. Thus the washing of the impressed gelatine film has the effect of producing an image in relief; for we have a photograph on gelatine, not made up of light and shade, but of depressions and hollows of various depths. This gelatine image, which, it must be remembered, has a stout backing of collodion to give it strength, is next put into a strong solution of alum, which has the effect of tanning and fixing the image, rendering the whole more permanent. This matrix or mould is next dried, and is then ready to furnish the engraved plate. A sheet of type metal, or lead mixed with a small percentage of antimony, is placed face to face with the gelatine matrix and subjected, in a hydraulic press, to an even, steady, and very heavy pressure; the result being that the gelatine, without being injured in the slightest degree, is pressed into the type metal, which receives a counterpart image similar, down to the most

minute details, to that upon the gelatine matrix. The latter, which might be deemed the most delicate of the two substances, and the most ready to give way, is, strange to say, so free from injury after the process that it will serve for the purpose a score of times; so that, the matrix once secured, there is scarcely any limit to the number of engraved plates which it will furnish. The engraved plate, as we have said, is of precisely the same nature as the gelatine film, only, of course, the picture is reversed, and the prominences and depressions have changed.

The engraved plate is put into a press ready for printing, and a sheet of thin paper, which has been submitted to considerable pressure, and thus rendered of uniform thickness, is put in position under it; upon the paper is poured a little transparent gelatinous ink in a warm state, the same being of such a nature that a thick layer of it appears black, while a thinner layer is only dark or light brown, according to the amount of ink in the film. A little pool of this ink is poured upon the paper which is to receive the impression, and the printing block then descends and presses out all that is superfluous. The block is not raised again immediately afterwards, but is allowed to remain for about a minute, to allow time for the ink to set; and during this period the printer may turn his attention to other printing presses. After an interval the block is lifted, and we have then an impression upon paper similar in detail and half tone to an ordinary silver print. In the deep shadows of the picture there is a thick layer of the dark transparent ink, while in the half tones the layer is thinner, and consequently lighter; for it must be borne in mind that the shadows of the image upon the engraved plate are represented by deep hollows, and consequently these allow a thick layer of ink to remain, when the block descends and squeezes the pool of ink from under it; and so in like manner with the half tones, where the depressions in the plate are less. The print is formed of ink made up for the most part of gelatine and Indian ink, or other suitable pigment; and in order to render it more permanent, it is dipped into an alum solution to tan the gelatine.

Woodburytype prints may be produced of so fine and delicate a nature as to be quite indistinguishable from silver prints; and as in pigment printing, they may be produced of any desired colour, according to the kind of pigment introduced into the ink. There is one serious drawback in this production at present, however, and that is the impossibility of furnishing prints beyond a certain size—say 10 or 12 inches square. This is due to the great difficulty that exists of obtaining metal plates of large size absolutely uniform in thickness and in evenness of surface. As the tone of a picture depends solely upon the uniform pressure of the block against the paper, any unevenness in this respect causes a portion of the print to be darker or lighter in colour. The *desideratum* is, of course, more easy to secure in the case of small pictures than large. The rapidity with which these photo-mechanical prints can be produced is unlimited; for once the gelatine matrix is secured, no further aid from daylight is necessary, and the preparation of engraving blocks and the printing off of copies can be proceeded with without delay. Woodburytype is, we repeat, the most perfect photo-mechanical printing process known at the present day, and produces pictures more closely allied to silver prints than any other.

Collotype Printing.—Collotype printing, or printing from a colloid film, differs much from photo-lithography, where the impressions are pulled off a stone or zinc surface. In photo-lithography only black lines can be produced, such as are to be found in engravings, drawings, and the like; but in collotype printing, whether termed *Lichtdruck*, *Albert-type*, *Heliotype*, &c., half tones can be obtained. It is a photo-mechanical process, therefore, producing every gradation of tone, like Woodburytype. It is a less expensive process than the latter, and will yield prints of much larger dimensions; but these are scarcely so vigorous and sharp as those by the Woodbury process.

Photo-collotype, like Woodburytype and pigment printing, requires the employment of gelatine and bichromate of potash. The essential principle upon which collotype printing rests was first pointed out by Poitevin and Pretsch—viz., the property of bichromated gelatine, after exposure to light under a negative, to repel or attract in parts a greasy ink rolled over its surface. Tessié du Motay may be said to be the first who invented a practical photo-collotype process, the only drawback to his invention being the fragile character of the printing blocks produced, these being broken up and ruined before a hundred prints could be pulled from the surface. The gelatine surface which printed off the impression could not be backed up with sufficient firmness to withstand the great pressure to which it was subjected. Tessié du Motay's plan was to take a mixture of gelatine, gum, and isinglass, and support the same upon a copper plate. This copper plate played an important rôle in the process; for by using, in conjunction with the trichromate (employed instead of bichromate as being more suitable when thick surfaces are to be sensitized), a reducing salt, a reaction was brought about upon the organic compound, rendering that portion of it in contact with the metal perfectly insoluble—a result accelerated by warming the plate prior to its being placed upon the metal. In this way Tessié du Motay succeeded in establishing, between his sensitive surface (that was to be solarised and subsequently inked up) and support, an insoluble layer, which, while serving to attach the printing block to its foundation, and acting as a kind of medium or buffer, was at the same time perfectly incapable of absorbing moisture during the manipulation of the plate in the lithographic press. The gelatine surface was exposed under a *cliché*, and then put into the press for printing from, the image being moistened with a wet sponge and inked up as in lithography.

The reason of the plates breaking up was doubtless the fact that the gelatine mixture was not so uniformly cemented to the metal plate as the inven-

tor hoped, and this difficulty Albert overcame in his process. Instead of a copper plate as a support he employed a sheet of patent plate glass, coating one side of it with a bichromated gelatine mixture, then laying it prepared, face downwards, upon a sheet of black paper, and exposing it to the action of light from the back. The black paper absorbed the rays from the surface touching it; and thus, while the greater portion of the film was rendered insoluble, the exterior surface remained unacted upon, and capable of adhering to the second sensitive film subsequently placed on the top of it to receive the image, and become in course of time the printing block. By employing glass the great advantage was obtained of being able to watch and control the action of the light, and insure the production of an insoluble layer in bitumen, which cemented the image firmly to the glass plate.

The *Lichtdruck* process is very similar to Albert-type; but *Heliotype* is somewhat different, chrome alum being employed with the gelatine to render it insoluble in water, although still capable of absorbing moisture. In heliotype the gelatine mixture is prepared in the form of skins, and these are exposed to light and cemented to a metal or stone basis for printing from.

The collotype process, as practised by Captain James Waterhouse, the assistant surveyor general of India, gives remarkably good results, and we shall therefore describe it in detail. It is similar to the heliotype, Lichtdruck, and Alberttype, the printing surface being a layer of insoluble gelatine which has been acted upon by light, through the agency of an alkaline bichromate, in such a manner that the parts exposed to light become non-absorbent of water in proportion to the degree in which they have been acted upon, while the protected parts absorb water in proportion to the amount of protection they have received. If the surface be wetted, and a roller charged with printing ink be passed over its surface, the exposed parts will attract the ink exactly in proportion as they are non-absorbent of water, while the unexposed and fully absorbent parts will repel the ink exactly in the same manner as the wet parts of the stone in lithographic printing. The practical working of the process may best be considered under four heads:—1st, the original drawing; 2nd, the negative; 3rd, the preparation of the printing film; 4th, the printing.

The Original Drawing.—The great advantages of the photo-collotype process over ordinary photo-lithography is that any drawing or sketch, whether drawn in lines only, or coloured in washes that will give a good photograph, may be reproduced by it; while photo-lithography, as already pointed out, can only reproduce designs in black and white. At the same time, in this process it is necessary that the drawing to be reproduced be well and accurately executed, otherwise the copies will be unsatisfactory.

The Negative.—As the printing surface receives the image direct from the negative, and not by transfer as in photo-lithography, the necessity for the negative to be reversed will be easily understood. There is no difficulty in obtaining reversed negatives by either of the three following methods:—

1. By the use of a reversing mirror in front of the lens:

2. By taking the negative through the glass-plate instead of on its surface, *i.e.*, by turning the glass in the camera so that the collodion film may be turned away from the lens instead of facing it:

3. By coating an ordinary negative with gelatine, or transfer collodion, and stripping it off the glass.

The first plan is a good and simple one; the second answers well if the glass plate can be obtained free from bubbles and other imperfections. The third plan will not do well where mathematical accuracy is required, as the gelatine is apt to contract; but in any other case it may be employed with advantage. The best plan to strip off a negative film is to carefully put it on a levelling stand, and surround the plate by a wall of putty or dough. A solution of gelatine composed of—

Gelatine,	1 oz.
Water,	8 ozs.
Glycerin,	1 drachm

is poured upon it, and left to dry in a place free from dust; as soon as the film is dry, a knife is run round the four sides, and the film instantly peels off the glass. If the gelatine film receives a coat of collodion to which a little castor oil has been added, it is proof against any atmospheric influence. A plan suggested by Captain Abney, R.E., of transferring the negative films by means of india-rubber solution and transfer collodion, and then laying them down reversed on a glass plate, is most successful, and obviates many difficulties.

Preparation of the Printing Plate.—The printing plates are of glass, ordinary plate glass about three-eighths of an inch in thickness answering very well. The plates are ground on one side with very fine sand. When required for use they are thoroughly cleaned in the usual manner, and carefully levelled by means of tripod levelling screws placed so as to form an isosceles triangle corresponding to the size of the plate; this method is much more convenient than using the ordinary levelling-stands.

While the plates are being levelled, the gelatine solution is prepared as follows:—

A	Gelatine,	1 oz.
	Sugar,	1 drachm
	Distilled water,	6 ozs.

Heated in a water bath till the gelatine is dissolved.

B	Honey soap,	30 grains
	Distilled water,	1 oz.

Boiled till the soap is dissolved.

C	Tannin,	10 grains.
	Water,	1 oz.

The above quantity will be found sufficient for two square feet of plate.

As soon as the gelatine solution A is quite ready, solutions B and C are mixed together hot, and poured gradually, with constant stirring, into A. The whole is then strained through two thicknesses of coarse

cotton cloth, and poured evenly over the plates, any bubbles being removed with the point of a penknife. The plates are then covered over with a light paper cover to prevent dust falling on them, and in the cold months will *set* firmly in about an hour, when they may be removed into the open air and turned face downwards upon small blocks of wood at their corners to remain till quite dry, which will be in from twelve to twenty-four hours. In the hot weather, however, they will neither set nor dry so readily, and it will be advisable to increase the setting power of the gelatine by substituting 1 oz. of spirits of wine in place of the water used in dissolving the tannin.

When the plates are dry, they may either be put away till required, or sensitized at once in a bath of—

Bichromate of potash,	1 part.
Water,	20 parts.

They are allowed to remain in this for about five minutes, and are then removed to a drying-box and dried with a gentle heat. When dry, the deposit at the back of the plates, as well as any inequalities at the corners of the gelatine film, are removed, and the plates are ready for exposure to light under the negative.

This operation is performed in a pressure-frame, in the same way as for ordinary photographs. It is advisable, however, to secure clean margins by shielding the borders of the negative by means of a mask cut out in yellow or brown paper, which should well overlap the edges of the printing plates. The mask is laid on the glass of the pressure-frame; then the negative in its proper position (should this be a transferred film, it is advisable to place a glass plate between it and the mask, in order to secure the most perfect contact); the sensitive plate is then rubbed over with a little powdered soapstone, to prevent its adhesion to the negative, and adjusted in its place over the negative, covered with a sheet of black velvet or brown paper, over which a thick glass plate is laid, and, if necessary, a few sheets of thick paper to give a good strong pressure, when the bars are shut down. The thick plate of glass has been found to give much sharper and more even contact than the usual backboard.

The amount of exposure to light varies from about ten minutes in the sun for a clear line subject, to from twenty-five to fifty minutes for a subject in half tones, according to the nature of the negative and the intensity of the light. As there is some difficulty in estimating the amount of exposure necessary—for the impression cannot be referred to during the printing—it is well to have recourse to an actinometer, such as that described in the section on Pigment and Carbon Printing.

When the exposure to light is considered sufficient, the negative and mask are removed, and the *back* of the sensitive plate is then exposed to light for about five or ten minutes, to thoroughly harden the gelatine and prevent it from swelling too much in the after processes. It is as well to carry on this second exposure under a piece of ground glass, otherwise, if there should be any scratches on the back of the sensitive plate, or on the glass of the pressure-frame, they will show as white lines on the print; after this, the plate is taken out of the frame, a little tallow is rubbed round the edges to prevent water getting underneath and stripping the film, and it is then plunged in water and thoroughly washed till all traces of bichromate have been removed, and is then ready for printing.

The Printing.—The plate may be printed in the lithographic press, and in this case requires to be fixed on a level stone with plaster of Paris. Vertical pressure is, however, better, and the Albion press answers the purpose well; the bed of the press being fitted with two or three thicknesses of kamptulicon, besides a sheet of vulcanized rubber on which the plate rests. It is also desirable to place a sheet of white paper over the bedding, in order to enable the printer the better to see the state of the plate when it is being inked up. The plate, having been well soaked in water, is laid on the press, and after being wiped to remove the excess of moisture, is inked in, if a line subject, with an ordinary lithographic roller charged with an ink composed of lithographic chalk ink, thinned with a little olive oil, followed by a rolling with a smooth roller to clean away the superfluous ink. A mask of the required size is laid on the plate; over this comes the printing paper, covered with a piece of soft felt to drive the paper well into the hollows of the plate; the tympan is lowered, and the impression pulled in the ordinary way. The plate is then damped, and the work goes on in the same manner without difficulty.

For printing in half tones the process is somewhat different, and to obtain uniformly successful results requires considerable skill and experience. The plate is first inked in with a small leather hard roller charged with stiff ink (rendered stiffer, if necessary, by the addition of a little Canada balsam), which adheres only to the deeper shadows; the half tones are then brought out by rolling in with a smooth lithographic roller, charged with a lighter and softer ink. Rollers composed of glue, treacle, soap, and catechu have been found useful in certain cases, but on the whole lithographic rollers are to be preferred. The impressions are best printed upon an enamelled paper, or one having a smooth glazed surface.

Before putting away the plates after printing they should be washed with turpentine, followed by a very weak solution of caustic potash to remove all traces of the greasy ink; they may also be treated after this with a mixture of gum and glycerin with advantage.

For clearing the image after it has been inked up, an aqueous solution of citric acid will be found useful. Water containing 20 per cent. of acid is a good mixture; it has all the valuable properties of nitric acid and cyanide of potassium in clearing the surface of greasy scum, and at the same time makes the lines take the ink well.

It should be borne in mind that perfect results cannot be obtained unless the surface of the gelatine

printing block is in *absolute contact* with the negative during printing; and this cannot be secured unless the negative in the form of a film (detached from the glass, therefore) is laid upon the sensitive gelatine surface. This should always be done, if possible, the negative film being stripped from the glass in the manner already indicated. When the film has been obtained upon a layer of gelatine or india-rubber, the plan of operation is as follows:—The sensitized and dried gelatine plate, which is subsequently to form the printing surface, is covered with an extremely thin coating of wax (dissolved in turpentine or benzol), and is then put into a bath of spirits of wine. The negative film is laid upon the gelatine surface in its proper position, and then both are removed from the bath, and the film is pressed down by means of a sponge; a few thicknesses of blotting paper and a glass plate being put upon the film until dry. The gelatine surface is then exposed to light with the negative film upon it, and the latter is removed as soon as the printing is complete. If the gelatine surface has been well coated with wax, and the negative film is pretty tough, there is no difficulty in removing it, and it may be laid aside in sheets of blotting paper for future use. Should the film tear, or be difficult to remove, it should be dissolved off at once with ether or other solvent; otherwise, if left to soak in water there will be a continuing action of the light in the parts protected by the film, and they will print darker than the other parts of the plate, and spoil the impressions. Before the gelatine surface is put to soak the wax should be removed with a little turpentine; the image may then be washed aud inked up as already described.

Another formula for making the tanno-gelatine composition used for the printing plates is as follows:—

Gelatine,	30 parts.
Albumen,	30 "
Tannin,	1 part.
Water,	240 parts.

The addition of albumen is advantageous in rendering the film tough, and making it more adherent to the glass.

ENLARGEMENTS.—It is very necessary that the negative from which the enlargement is to be made should be most perfect in its character. Fine thin glass must be selected, free from every kind of imperfection, and the image produced must be soft and transparent. In no portion should it be very dense. A long exposure will generally give a plate of the required kind; it must, however, be quite free from fog, and perfectly transparent in the clearer portions. The image must be sharply formed, and appear clear and bright.

The enlargement may either be made in a copying camera, or by means of sunlight or artificial light reflected through the negative upon a screen. SOLOMON has constructed a magnesium lamp which answers the purpose, the negative being put into the apparatus in the same way as a slide is put into a magic lantern. To give the illumination magnesium wire is burnt, the same being regularly paid out by a clock-work movement. The image is focused and projected upon a screen, upon which is stretched sensitized paper. After the luminous image has acted for the period of a minute, more or less, according to the density of the negative, the paper is put into a developing solution and afterwards fixed. SOLOMON'S instructions as to formulæ are—

IODIZING SOLUTION.

Iodide of potassium,	80 grains.
Bromide of ammonium,	35 "
Chloride of ammonium,	10 "
Gelatine,	60 "
Albumen,	1 oz.
Distilled water,	10 ozs.

Mix and let the solution stand until the gelatine has become soft, and then apply heat until it has perfectly dissolved. The solution should be applied to the paper with a clean sponge.

SENSITIZING SOLUTION.

Nitrate of silver,	1 oz.
Glacial acetic acid,	½ "
Distilled water,	12 ozs.

When the paper has been iodized and dried, float it on this solution for five minutes, or it can be applied with a little cotton wool.

DEVELOPER.

Gallic acid,	60 grains.
Acetate of lead,	10 "
Distilled water,	10 "

Filter well. In cold weather the solution should be used warm.

FIXING SOLUTION.

Hyposulphite of soda,	10 ozs.
Water,	60 "

Dr. VON MONCKHOVEN recommends, for enlarging, an oxyhydrogen apparatus of his own construction, by means of which he obtains most excellent results. It may be employed for producing enlarged collodion negatives on glass from small glass positives, a few seconds' exposure being necessary. To obtain enlarged paper prints the paper is stretched on a screen as in the former case, the paper being first prepared with a mixture of—

Water,	1 litre.
Tapioca,	10 grams.
Iodide of potassium,	10 "
Bromide of potassium,	10 "

The tapioca is boiled in water and then passed through linen; the iodide and bromide are then added. The sheets of paper are immersed one after the other in this liquid, and are then suspended to dry; they are kept in a portfolio till required for use. The paper is sensitized by being plunged into a silver bath, or the liquid may be applied carefully by means of a tuft of cotton wool. Another plan, which is a good one with large sheets, consists in employing a large horizontal wooden tray on two pivots, by means of which the sensitizing solution poured upon the paper is rocked to and fro over the surface. The sensitizing bath is made up of—

Distilled water,	5 litres.
Nitrate of silver,	250 to 400 grams.
Citric acid,	20 "

After sensitizing the sheet is dried, although it may very well be exposed in a comparatively moist state to receive the impression. The paper is exposed until the heavy shadows are slightly seen, and the image is then developed by gallic acid. Two solutions are prepared and filtered, made up as follows:

A	Gallic acid,	100 grams.
	Alcohol,	1 litre.
B	Acetate of lead,	100 grams.
	Distilled water,	1 litre.

The best plan is to form the paper to be developed into a tray, and place it upon a developing board; or better still, in the rocking tray on pivots just mentioned. If the print is not very large, an ordinary porcelain dish may be employed. As many litres of water are put into the utensil as will suffice to cover the print, and then for every litre of water, 2½ c.c. of gallic acid (A) and 10 c.c. of glacial acetic acid, the utensil being rocked to mix the liquids. Then 2½ c.c. of the lead solution (B) are added, and the mixture again agitated. The solution should be perfectly clear, and not in any way turbid. The print is not washed, but is introduced as uniformly as possible into the liquid, rocking the bath, meanwhile, so that the sheet is constantly bathed; otherwise, spots and stains upon the print will be produced. The time of development varies from ten to forty minutes; the developing solution being poured away and replaced by water.

The best enlargements are, however, produced by means of an enlarging camera. A positive is first taken from the negative of the same size as the latter, this being done either by placing a dry sensitive plate against the negative, and letting the light act through for a second or so, and developing the plate in such a manner that a good vigorous *cliché* is the result; or the positive may be obtained, and this is by far the best plan, by carbon printing. A piece of carbon tissue is simply exposed under the negative, soaked in cold water, applied to a glass plate, and then developed; this makes a most suitable positive transparency for enlarging from, because it has far more vigour of a uniform character than a collodion film, and it is for this reason, indeed, that the latter never furnishes a thoroughly satisfactory enlargement. The transparent positive is placed in the camera, and by means of a suitable lens an enlarged image, this time a negative one, is thrown on the focusing screen. The camera is adjusted until the enlargement is shown to be of the required size, and then a collodionized plate is put into the apparatus, and a negative secured in the usual manner. Of course, if very big enlargements are desired, the camera must be a very long and spacious affair. The negatives, and consequently the prints produced by this method of enlargement, are soft and brilliant, and free from that disagreeable grain and coarseness which characterizes the ordinary enlargement. B. J. Edwards, whose method of enlarging is also a very perfect one, employs neither collodion nor carbon tissue in the production of his positive, but a sensitive composition which is kept a secret.

Photo-Enamels.—Most of the enamelling processes practised at the present day are secret methods. M. Poitevin, M. Tessié du Motay, M. Lafon de Camersac, M. Joubert, M. Grüne, M Leth, and MM. Geymet and Alker, abroad; and Messrs. Henderson, Mayland, Robinson and Cherrill, and others in this country, have brought the process to a very high degree of perfection. So delicate and risky is, however, the preparation and burning in of pictures of this kind, that it is natural that even skilful workers cannot work with uniform success; and it not unfrequently happens that a most perfect enamel at the very last stage of production cracks, or loses its agreeable tint, without almost any apparent cause. M. Leth, of Vienna, a good photo-enameller, proceeds in the following manner:—In the first place, a collodion positive is produced upon glass in the camera, or by means of a dry plate in the printing frame. This positive is covered with a solution of 1 gram. of gutta-percha in 30 grams. of chloroform, previously filtered. When cold the margin of the film is cut, and the same plunged into cold water, and in this way the collodion positive separated from the glass. It should be kept flat under pressure. As enamel surfaces are rarely flat, but generally convex, it is a matter of necessity that the collodion film should be on an elastic basis. Enamelled plates of a suitable character may be purchased, being of copper, covered with white enamel; they are oval, and possess a relief like a cameo. The surface of the enamel is well cleaned and polished, and then coated with a mixture made up in the following proportions:—

Distilled water,	100 grams.
Bichromate of potash,	6 "
Gum arabic,	5 "
Honey,	1 "
White sugar,	1 "

So long as this mixture is liquid, it is not sensitive to light. It must be filtered through Swedish filtering paper, an operation which proceeds very slowly. As it has the consistence of syrup it may be easily applied, after a little practice, to the curved surface of the enamel plate, the coating being afterwards dried at a gentle heat before a stove; this last operation must be carried on in the dark. The enamel plate, thus prepared, is covered with the film carrying the positive image. By carefully pressing the same down in every direction, the film is placed into perfect contact with the enamel; the operation being more facile if the film is rather larger than the plate, the edges of the former being pressed underneath the margin of the enamel. In this state the same is exposed to the action of sun-light for the space of one or two minutes, or in diffused light for a period of from five to fifteen minutes. To develop the image, it is taken into the dark room and the film removed, when a visible image will be found upon the prepared enamel surface. Finely ground pigment, as for instance, powdered charcoal, sprinkled over this exposed surface, adheres to those portions where the light has not acted; but instead

of charcoal, powdered enamel of any desired colour is employed, together with a flux of some kind, also in powder. M. LETH prepares his powder by fusing in a crucible a mixture of 2 parts of sulphate of cobalt, 1 part of sulphate of zinc, 2 parts of sulphate of iron, 2 parts of sulphate of manganese, and 12 parts of saltpetre. The product is reduced to powder and well washed. One part of this powder is mixed with 2 or 3 parts of flux, also reduced to powder. The flux is secured by calcining in a crucible 2 parts of sand, 1 part of borax, and 6 parts of red lead; the fusible glass thus produced being subsequently reduced to a fine powder. A flux containing no lead may be obtained by calcining in a crucible 8 parts of quartz sand, 4 to 6 parts of fused borax, 1 or 2 parts of saltpetre, and 1 part of chalk. To operate well the powders must be impalpable, and are either sprinkled upon the image from a bag, or applied over the surface with a soft camel's-hair brush. In the latter case a brush full of powder is taken, and commencing from the top, the image is dabbed over with it, any superfluous powder being afterwards removed by sweeping the brush over the surface. If the image appears too black, a too large amount of powder having become attached, the enamel plate is heated slightly over a spirit lamp, and the excess of pigment powder removed by means of a fresh brush. If, on the other hand, the amount of powder attached appears too small, it is well to breathe on the surface of the image, and apply a further quantity of powder.

The enamel is next immersed in sulphuric acid diluted with twice its volume of water and alcohol, which has the effect of eliminating the soluble salts of chromium, which impart a yellowish tint to the image. It is then washed in plenty of water and allowed to dry. The plate is then ready to be burnt. This is done in a small muffle-furnace; the image upon the enamel plate loses a little during the operation, and may even disappear altogether if the temperature is too high, or the heat too prolonged. In the latter case the image becomes dissolved in the excess of white enamel covering the plate. Very handy and cleanly furnaces are now manufactured, burning petroleum or gas, and these are very suitable for enamelling. The temperature to which the enamels should be exposed is that of a cherry red colour, and this ought never to be passed. The enamel is put upon a metal plate in the red-hot furnace, and allowed to remain therein for not less than a few minutes.

Another method of producing enamels is simply to attach a collodion film, carrying an ordinary silver image, to a porcelain or enamelled surface. This silver image may be burnt in, by putting the same into a muffle-furnace, or if desired, the silver picture may be changed into gold, platinum, or iridium, by immersing it in a solution of the salts of these metals. When the image has been burnt in upon the surface, it assumes the colour of the metal of which it is composed.

J. SOLOMON gives two methods for producing this most beautiful and permanent form of photograph. He calls them the powder process and the film process; and both depend upon securing good transparencies, or photographic *clichés*, on a supple film. The transparency best suited for the powder process is, however, entirely unsuited to the film process. In the former case it must be fully developed, with high lights full of detail, and look well by transmitted light, the image serving for any number of proofs; in the film process each enamel requires a transparency, the film being transferred to the enamel tablet. In this case the film *cliché* must appear best against a white background, the high light being transparent, so that the white ground behind shows through, and the blacks rich and opaque. The developer recommended to be used for producing the collodion transparency for the film process is—

Pyrogallic acid,	3 grains.
Citric acid,	3 "
Glacial acetic acid,	15 minims.
Water,	1 oz.

Or,

Proto-sulphate of iron,	10 grains.
Gracial acetic acid,	12 minims.
Water,	1 oz.

Slow development is best, and the iron developer should only be employed in the case of a very dense negative, and then only in the first stage of the operation. To produce the transparency for the film process, a copying camera must be employed.

In the powder process the following solutions should be prepared, not being mixed together until actually required, as they are then sensitive, and must be kept in the dark room:—

FORMULA I.

a	Dextrine,	1 oz.
	Grape sugar,	1 "
	Finest powdered gum arabic,	1 drachm.
	Distilled water,	10 ozs.
b	Bichromate of ammonia,	1 oz.
	Distilled water,	10 ozs.

FORMULA II.

a	Best honey,	8 grains.
	White sugar,	15 "
	Gum arabic,	1 drachm.
	Glucose,	1 "
b	Bichromate of ammonia,	5 ozs.
	Distilled water,	½ oz.

When required for use, *a* and *b* are mixed in equal proportions and filtered.

A well cleaned glass plate is coated (in the dark room, of course) with either of the sensitive compounds mentioned, and drained on blotting paper; it is then placed, while still in a slanting position and upon the blotting paper, on an iron plate, under which is a spirit lamp, for the purpose of gently drying the film. When hard and dry, it is covered with the transparency (film against film) and put into a printing frame, the time of exposure being judged by a trial plate—in sunlight thirty seconds being enough, while in dull light half an hour is not too much. The pressure frame must not be allowed to be damp and cold in unfavourable weather, and the development must take place in a warm room.

The plate is held in the left hand, and black vitrifiable powder, made up of—

Hard black China,	100 parts.
Brown-purple,	40 "
Ground up for use,	

is strewn over it, the plate being shaken to scatter the powder all over it. The powder is brushed to and fro with a camel-hair mop, and then the plate allowed to remain to be influenced by the humidity of the atmosphere. The operation of dusting may be repeated three or four times till the image is brilliant; and it is well to treat several images at the same time, and then select the best for vitrifying. Coat the plate then with plain collodion, and as soon as this has set, the margins of the film are rubbed off with the finger nail; it is then immersed in water, acidulated with a little hydrochloric or nitric acid, which eliminates the bichromate and loosens the film. After remaining here for some time, the plate is transferred to pure water, where the image is floated off the glass and reversed in the water, so that the collodion side is downwards. The enamel plate having been washed in carbonate of soda to remove greasiness, is carefully put under the floating film, the film being adjusted on the surface by the aid of a soft brush—both surfaces being withdrawn from the water when they are in proper juxtaposition. The margin of the film is bent round underneath the enamel to make it adhere more closely. The heating of the enamel in the furnace is a difficult operation; the heat should be ardent and equally distributed over the surface of the enamel, the colour being a cherry red. Solomon is very particular on this point. The draft hole must be stopped before placing the tablet in the muffle, so as to prevent a current of air from that quarter, and the room door must be closed for the same reason. When nearly ready, place inside the muffle one of the cylindrical lumps, and upon it the hollow hemisphere of clay, whereon the disc which carries the tablet in the furnace is turned. Then take one of the largest circular plates of fire-clay, cover it with whitening to form a bed on which afterwards to place the enamel, and transfer it with the tongs to the hemispherical disc in the muffle, and leave it till well heated. Remove and lay it on a piece of fire-clay, while the tablet is placed on its centre. Then return to the muffle, and watch carefully the result. The tablet heats very rapidly, the collodion film burns away, the image will disappear, but will quickly re-appear with some parts brilliant, indicating fusion. The disc is turned slowly round, so that parts may be influenced by the heat; and when the picture is brilliant all over and the fusion complete, the tablet must be instantly removed.

Fluxing the image gives increased brilliancy; and as recommended by Tunny, should be performed as follows:—"Take as much flux as would lie upon half a crown, grind it up in a small mortar in half an ounce of spirits of wine, and add this to half an ounce of ordinary normal collodion; this forms the glazing emulsion. When you have subjected the enamel tablet with its image to a sufficient heat in the mouth of the furnace to destroy the collodion film, lay it aside until cool; then take the bottle containing the enamel emulsion (which must always be shaken before use), and pour over its surface in the same manner as you would a collodion plate. Have a little bit of blotting paper ready to lead off the last drop, in order to avoid the thickening which would otherwise take place, and cause thereby a transparent mark. The surface now presents a perfect coating of enamel glaze; when dry pass it into the furnace, and in a very short time it will become vitrified, giving to the surface a most perfect brilliancy." In the film process the transparency having been produced, is treated in an acidulated bath and removed from the plate; and after washing, it is toned in a bichloride of platinum, and fixed in a hyposulphite solution. The image is not reversed, but simply transferred to the tablet, and burned as before described.

Recovery of Waste Silver and Gold in Photography.—Monckhoven, in his "Treatise of Photography," goes very fully into this subject, for, as he points out, it is one of extreme importance, seeing that 90 per cent. of the precious metals employed are to be found in the residues. Silver residues are to be found in the filter paper which has served for filtering silver baths, in the paper employed in wiping out glass slides, in old unfixed prints, and in cuttings from untoned pictures. All these papers should be burnt, not in too dense a heap, but loosely, so that a white ash, and not a black one, is secured. Next there are the old hyposulphite or fixing baths, which contain silver, and these are collected in a large barrel, which should have a stop-cock of copper pierced in the side about 8 inches from the bottom. When the cock is full, put in a solution of "liver of sulphur," which will precipitate the silver. The danger to be avoided here, is not to add an excess of "liver of sulphur;" and to avoid this, when the deposit has been formed it is well to take a little of the liquid in a test tube, and add to it some of the sulphur compound to ascertain if all the silver has been thrown down. If the addition of a few drops produces no turbidity, then make the reverse experiment, taking another sample of the liquor and adding to it a little solution of silver. If a precipitate is then formed, you have an excess of sulphur, and then you must add some more old hypo bath and allow it to deposit. Without these tests are made, either the whole of the silver is not precipitated, or a portion of the precipitate has become re-dissolved in the sulphur. After a few days the liquid is drawn off from the top; and when sufficient residue has been thus collected, it is taken out and dried. Another cask or pan should be devoted to the receipt of all old silver baths, washings from the prints before toning, rinsings of utensils which have contained silver solution, and indeed all liquids but those of the fixing baths. When this vessel is pretty full, a large piece of copper sheet is put into it for a day, and the abundant precipitate formed is allowed to subside. Then take a little of the liquor in a test tube, and

add a drop or two of hydrochloric acid. If a precipitate is formed, the copper plate must still remain in the bath; and this it is allowed to do until no more precipitate is formed on testing with hydrochloric acid. Then pour off the liquid, and filter the residue.

From old gold toning baths the precious metal is thus recovered. Pour into the collected liquid, which is often turbid by reason of gold in fine black powder precipitated in it, some common muriatic acid, until the liquid assumes a decided yellow colour. Dissolve some sulphate of iron in ten times its bulk of water, filter the solution, and add it to the gold liquid, in the proportion of 100 c.c. of the former to a litre of the latter. The gold will immediately be precipitated. Allow the precipitate to be deposited, decant off the waste liquid, and collect the precipitate upon a filter. Let it dry thoroughly, and then it is ready to be reduced to a metallic state. We now proceed to describe how this should be done:—

The residue from the gold toning baths, as also the ashes from paper cuttings, to which we have referred above, are put into a crucible with half their weight of dry carbonate of soda and a fifth their weight of sand, and the vessel is placed in a good furnace. The reduction will take place at a comparatively low temperature. The silver will be recovered in a pure ingot which is completely soluble in nitric acid, while the gold alloyed with silver remains in the crucible in the form of a black powder. In dealing with the sulphide of silver (from fixing solutions) the operator should be very careful, for it will detonate if mixed with saltpetre in a mortar; the saltpetre should be first powdered, therefore, and mixed with the sulphide by hand, one part of the latter to three parts of the former being taken. Put the mixture into a crucible heated to bright redness, in instalments of from 15 to 20 grams. at a time, and wait an interval of a minute or two between each addition. When all has been introduced, the crucible is thoroughly heated in order that one single ingot may be formed. Let the crucible cool on the fire, and then break it up and secure the metal; the latter may be dissolved in nitric acid to give a nitrate of silver; and if there is any gold, this will remain in the acid in the form of a black powder. The chloride of silver is reduced by preparing an intimate mixture of—

Dry chloride of silver,	100 parts.
Carbonate of lime,	70 "
Carbon,	4 "

This mixture is heated in a crucible to a red heat for an hour at least, and when cool the vessel is broken, and an ingot of pure metallic silver is secured. It should be borne in mind, that before residues are placed in the crucible, they must be most carefully and thoroughly dried.

PIGMENTS.—Pigments are coloured powders, insoluble in water, which, when mixed with size, gums, oils, or varnishes, form paints. They are derived from both inorganic and organic sources. Under the former are included minerals and such chemical products as owe their colouring power to metallic and other salts; the latter derive their tints from animal or vegetable sources. As a general rule, the latter are more fugitive than the former. Some pigments are opaque, some semi-transparent, and some transparent. All these qualities are useful, especially to the artist, and depend for the most part on the aggregation of the particles of the pigment. The same body, chemically speaking, may vary considerably in these respects, according to the mode adopted in its preparation. When ground with oil or varnish some pigments have the quality of quickly oxidising the vehicle, or allowing of its quick oxidation, whilst others retard this oxidation. They are said to be good or bad dryers, accordingly. With bad dryers artificial aids are resorted to. Amongst the substances employed as siccatives are acetate of lead, lime, sulphate of zinc, and oxide and borate of manganese. Other substances have this siccative property, as burnt alum. This subject opens out for the chemist a large and remunerative field for investigation, and the direction in which this should be carried on seems to be that of the state of hydration of the pigments and their hygroscopic character. The good dryers now in use, unfortunately, in most cases interfere with the delicacy of the tint of the pigment, whilst those which do not are inferior in siccative properties.

Pigments should invariably be fine in texture. This quality is brought about, in such substances as are not naturally in fine powder, by grinding and levigation; but some substances formed by precipitation are already in the form of impalpable powder. Millstones arranged in different well-known ways are usually employed for this purpose. The material is ground in a stream of water, which carries off the fine portions into settling tanks arranged in succession. The rougher grains are deposited in the first tanks, and require regrinding; the lighter parts remain longer in suspense in the water, and flow on to larger tanks, where they are deposited after some time of rest. There are also other methods of grinding, a description of which hardly comes within the scope of this article. When pigments are intended to be made into oil paints, it is generally necessary to dry them after grinding. With many substances great care is necessary in this operation, as an elevated temperature either destroys their tone or materially changes their character: the carmines are an excellent illustration of this. The best method of heating drying chambers is that supplied by PERKINS, as by it high and regular temperatures can be obtained. The use of the word *body* in connection with pigments is somewhat ambiguous. When applied to opaque pigments, such as white lead, Naples yellow, &c., it is usually understood to signify density and covering power; when applied to transparent colours, as Prussian blue, &c., it would seem to mean tinctorial power.

In the following pages pigments are treated of individually. Their manufacture, chemical composi-

tion, properties, and the adulteration found in the commercial products, are entered into at length.

Whites.—*White Lead, Ceruse.*—This important white pigment, for which hitherto the science of chemistry has scarcely found an efficient substitute, is a carbonate of lead more or less basic, according to the process by which it is manufactured. For a description of most of the processes by which the pigment is made, see article Lead.

There are many other modifications of the manufacture of white lead which present no great novelty, or only produce an inferior article—inferior because the tint is bad, and because the covering power is imperfect.

In whatever manner white lead is prepared, it is found to be a carbonate of lead more or less basic. It would appear, on a review of the different analyses given by chemists who have devoted much labour to ascertaining the exact composition of this pigment, that seldom is a specimen found to correspond exactly to a definite chemical formula. Twenty-seven samples of Holland manufacture, examined by Vlaandern, gave the following results:—

	I.	II.	III.	IV.	V.
CO_2	11·4	11·4	12·4	12·2	12·0
H_2O	2·3	2·4	2·0	2·1	2·0
PbO	86·4	86·5	85·0	85·6	85·9

	VI.	VII.	VIII.	IX.	X.
CO_2	12·4	12·0	12·3	12·3	12·0
H_2O	2·1	2·0	2·1	2·3	1·8
PbO	85·7	86·1	85·4	85·5	85·6

	XI.	XII.	XIII.	XIV.	XV.
CO_2	12·3	12·2	12·7	12·7	12·5
H_2O	2·1	2·0	2·3	1·7	2·1
PbO	85·5	85·6	85.2	85·5	85·8

	XVI.	XVII.	XVIII.	XIX.	XX.
CO_2	12·7	12·5	12·9	12·9	13·1
H_2O	1·9	1·9	1·2	2·1	2·0
PbO	85·4	85·7	85·3	85·1	83·4

	XXI.	XXII.	XXIII.	XXIV.	XXV.
CO_2	13·5	13·5	13·2	13·0	13·3
H_2O	1·5	1·6	1·7	1·8	1·8
PbO	84·7	84·9	85·2	85·2	85·1

	XXVI.	XXVII.
CO_2	13·2	13·1
H_2O	1·9	2·0
PbO	85·0	85·1

The first two of these samples nearly correspond to a composition which may be represented by the formula, $PbH_2O_2 + 2(PbCO_3)$, the next ten would seem to have 2 parts of the hydrate to 5 of the carbonate, thus, $2(PbH_2O_2) + 5(PbCO_3)$; the next seven approach to the formula, $PbH_2O_2 + 3(PbCO_3)$; and the remaining eight specimens to the formula, $PbH_2O_2 + 4(PbCO_3)$. If we consider the rationale of the manufacture by the Dutch process, this variable composition will not appear strange. The action commencing on the surface of the crates, gradually penetrates to the interior; and it frequently happens that a crate is not thoroughly attacked, a core of metallic lead remaining beneath the crust. We may represent the action step by step thus:—The surface of the lead is oxidised by the combined action of the oxygen of the air and moisture; the vapours of acetic acid rise as the stack becomes heated and dissolve this oxide, forming basic acetate; carbonic acid, generated by the fermenting tan, decomposes the acetate, forming neutral carbonate of lead, and leaving neutral acetate to dissolve more oxide of lead. The basic acetate acts back on the neutral carbonate, forming a basic carbonate. This latter reaction was first pointed out by Barreswill, who showed that when neutral carbonate of lead is added to basic acetate of lead, basic carbonate of lead results. This action continues to the interior of the crate. The same explanation holds good in the precipitation processes.

White lead of commerce is frequently adulterated; when sold as a paint it is usually mixed with some foreign ingredient, though the best manufacturers send it out in a perfectly simple state. For this purpose, sulphate of lead, sulphate of baryta, sulphate of lime, and carbonate of lime are used. When a paint has to be examined, it is necessary to remove the oil. This is a tedious process. It may be accomplished by treating the paint with successive quantities of benzol, and allowing the pigment to subside, and decanting the benzol. After two or three washings, the benzol should be tested for oil. This may be accomplished by evaporating a small quantity at a gentle heat in a watch glass; if there is a greasy residue, the washing must be continued. When the oil has been satisfactorily removed, the pigment may be dried on filter paper. Pure white lead is perfectly soluble with effervescence in dilute nitric acid. A specimen, therefore, when treated with this reagent, should wholly pass into solution; if there is any residue, it may be lead sulphate, barium sulphate, or calcium sulphate. Calcium carbonate would, however, pass into solution with the lead. To determine the nature of the insoluble residue, it is necessary to wash it well on a filter to free it from any traces of nitrate of lead. If it be then treated with potassium bichromate, sulphate of lead, if present, will be changed into yellow chromate, which will remain when the excess of bichromate of potash is completely washed away. Sulphide of ammonium will change sulphate of lead into black sulphide. It is then easily changed into chloride by strong hydrochloric acid, and becomes soluble in boiling water. After removing all traces of lead by this method, if there is still a residue, it may be barium sulphate and gypsum (ealcium sulphate). By boiling for some time with a large quantity of nitric acid, the gypsum may be separated from the baryta, and may be detected in the clear solution by adding chloride of barium, when, if sulphate of lime were present, there will be a precipitate of barium sulphate. If after this treatment there is still left a white residue, it may be safely considered as barium sulphate. It is hardly necessary for the purposes of this article to enter into details of the verification of this. To detect an admixture of chalk or carbonate of lime, the solution in nitric acid should be treated with sulphuretted hydrogen until there is no further precipitation of sulphide of lead; then, after filtration, the filtrate should be neutralized with ammonia, and ammonium oxalate

added. A white precipitate of calcium oxalate, resoluble in acetic acid, will demonstrate the presence of chalk in the pigment.

The merits of white lead, as a pigment, are its good covering power and the ease with which it can be worked. This latter quality is no doubt due to its saponifying with the oil used as a vehicle. It is well known both to house painters and artists that the body, or opacity of this body, is lost in process of time. When applied on a dark colour so as to completely cover it, although at first it presents a surface of pure white, it gradually, in course of time, begins to grow semi-transparent, and permits the colour beneath it to be clearly seen. This is due to the fact that the fatty acids of the oil drive off carbonic acid from the white lead, and form a translucent lead-soap known as lead-plaster. The formation of this soap promotes the good drying properties of lead paint. Foul gas quickly blackens white lead, the sulphur usually contained in such gases uniting with lead to form black plumbic sulphide (PbS). In the trade there are pigments which go by the names of Venice, Hamburg, and Holland whites. The first is a mixture of equal parts of sulphate of baryta and white lead, the second contains 2 parts of baryta, and the third 3 parts to 1 of white lead.

Zinc White, Zinc Oxide.—This pigment is equal in whiteness to white lead, but, unfortunately, is deficient in body. It is not attacked by sulphuretted hydrogen nor by other deleterious gases. As a paint it does not affect the vehicle as white lead does; specimens in the author's possession have been exposed to the influence of a laboratory atmosphere for years, and are still as brilliant as when first laid on the canvas. It is a bad drier; but this can be remedied by using a siccative, like dry sulphate of zinc, also called white vitriol, which does not affect the colour in the slightest degree. It is now manufactured on a large scale, and could the quality termed "body" be imparted to it, without doubt white lead as a pigment would be driven from the market.

In its manufacture, metallic zinc is heated until it is vaporized. The vapour, on coming into contact with air, burns, and the white zinc oxide is produced. Figs. 1, 2, and 3 represent the usual form of retort employed in this operation. It is a depressed cylinder of fire clay gradually tapering to the opening, shown in Fig. 3, which serves for the introduction of the metal and the escape of the vapour. It measures usually 28 inches long, 10 broad, and 6 high. The sides are $2\frac{1}{4}$ inches thick. Figs. 4, 5, 6, and 7 represent the sections and plan of the reverberatory furnace, in which a number of these retorts are arranged. The fire-place is at C. The flame passes over the cylinders, *a a a*, and passes by the flue, *d f g*, which communicates with the chimney stalk, *h*. Pipes, *s s*, opening in front of the mouths of the retorts serve to conduct the air, raised to a high temperature by the waste heat of the furnace, for the combustion of the zinc vapour. When the

Fig. 1.

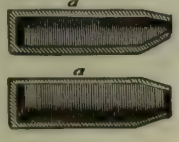
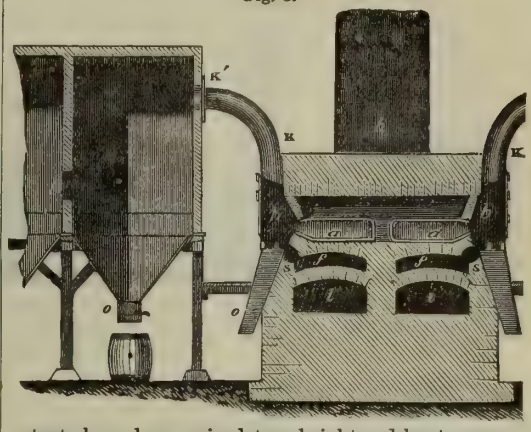


Fig. 2.

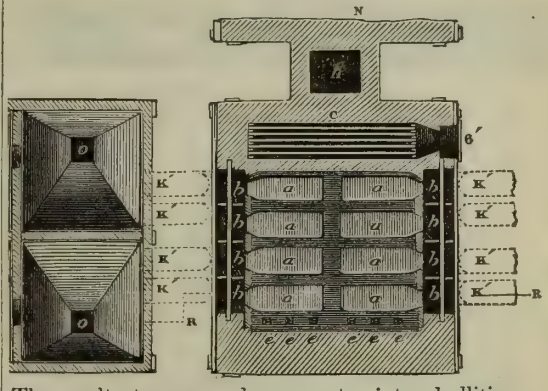


Fig. 3.



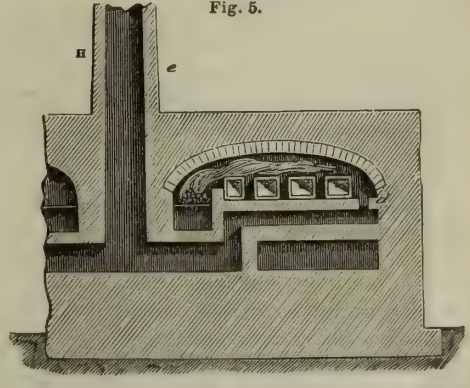
retorts have been raised to a bright red heat, one or two bars of metallic zinc are projected into each.

Fig. 4.



They melt at once, nd soon enter into ebullition. The vapour meeting with the air takes fire, and the

Fig. 5.



white oxide produced is carried by the air through the tubes, K K, into the collecting chambers, L L. The arrangement of these chambers is shown in Fig. 6, in which A represents the furnace, B B the pipes leading into the chambers, and G G the flues leading into the stalk H. There are usually four

condensing chambers for each retort, communicating with each by openings alternately at the top and the bottom of the partition walls. The last opening leading into the flue, G, is covered with a screen of

Fig. 6.

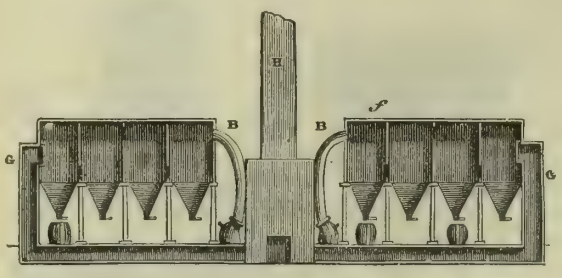
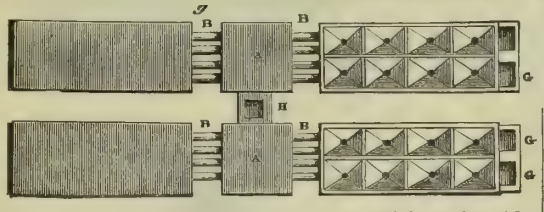


Fig. 7.

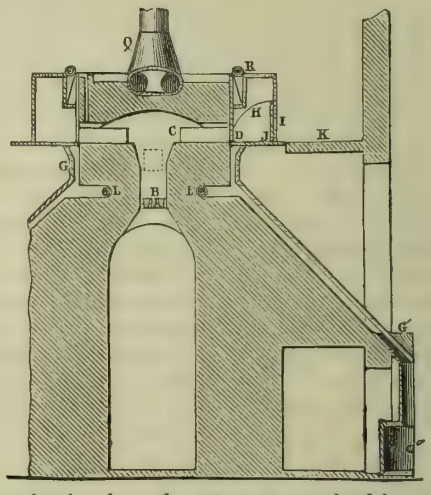


fine wire gauze to prevent any particles of oxide from being carried away. Other screens are also placed in the flue, G, all of which can be removed and cleaned when the meshes become closed with the fine powder. When sufficient oxide has been prepared, it can be easily removed from the walls of the condensing chambers through the openings in the hoppers beneath, which during the operation are kept closed with sliding doors. The oxide in the first chamber is usually impure, and has a greyish tinge. Besides impurities resulting from foreign bodies in the original zinc used, particles of metal which have escaped combustion are found. After sifting, the contents of this chamber are employed for an inferior pigment.

There are many modifications in the arrangements for the production of this substance; the method devised by M. Leclaire is worthy of mention. We transcribe the description and reproduce the engravings given in the article on Zinc in the earlier editions of this Dictionary, originally abridged from *Le Génie Industriel.*

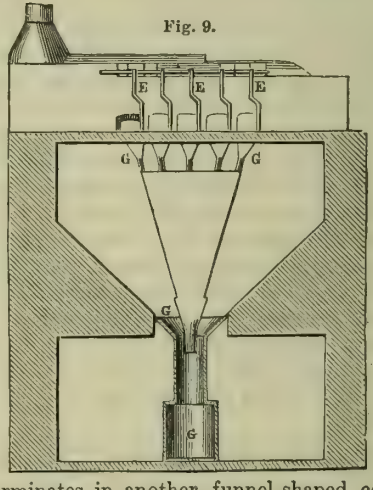
The Figs. (8, 9, and 10) show the distillatory furnace in longitudinal and transverse vertical sections and in plan. In these figures, A represents the fire-door, B the fire, and C the retorts, which are made of refractory material. Five are generally ranged at either side of the grate, but the number can be varied according to circumstances. The volatilized metallic vapours escape by the orifice, D, of the retort, before which are disposed a series of plates, E, called scrapers, attached to a horizontal iron rod, F, by similar pendant ones. By motion communicated by hand or machinery to the horizontal rod, the scrapers, E E, are moved backwards and forwards, and coming at each movement against the door of the retort, any oxide which adheres to the aperture is knocked off. The oxide and metallic

Fig. 8.



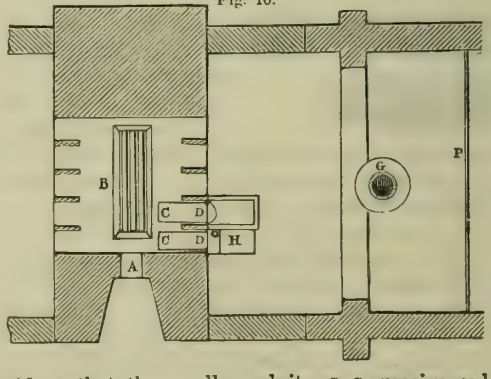
vapours issuing from the retort are received in small receptacles, G G, which open into an inclined channel

Fig. 9.



that terminates in another funnel-shaped conduit, G^1, and this leads them into the receiver, G^2. It is

Fig. 10.



evident that the small conduits, G G, receive only such matters as solidify in the mouth of the retort,

and which from their density cannot be drawn off to the receivers by the force of the current of gases passing through this arrangement to the chambers wherein the oxide of zinc is collected. A small plate-iron cage or box, H (Fig. 8), is fixed over the mouth of each of the retorts in order to isolate them. It rests upon a framework of metal, H^1, fixed into the wall of the furnace, and so constructed that it may be removed at will by means of a crane, or by making it slide or roll on a framework or small railway. The anterior aperture is directed towards the orifice of the retort, so that the products of the distillation empty themselves into it, and the posterior part has a door which may be opened at will. A trap-door, J, is contrived in the suspended plate, K, and which can be raised or lowered at will by an iron-wire rope passing through the posterior plate, I, of the box, H, without opening the door in this part of the latter. Sometimes, instead of lifting the trap-door, it is so formed that it can be drawn backwards when it is necessary to open it. K designates the suspended plate upon which the box or cage is placed; it is isolated in its construction from the chamber of oxidation. Currents of cold air may be directed upon this plate in order to cool it, so as to resist the temperature of the chamber. The hot air, admitted for the combustion of the metal, enters from the pipe, L; it communicates with the passage from the retorts to the receivers, and so drives the oxide of zinc formed into the latter. In the receivers the inventor places cloths for sifting or screening the products, the floor of each being a kind of hopper, or inclined plane, whereby the product gliding over the cloth is separated into its various qualities of fineness, and received at once into separate boxes placed beneath the sifter. In order to retain the finely-divided particles of zinc white which arise from the agitation, cloths are suspended at regular distances. These, while they afford a passage to the gases, retain the particles of metallic oxide, and so prevent a loss of material.

A draught pipe, Q, draws off the air and gases as well as the finely-divided oxide from the oxidising chamber through the whole arrangement. Another pipe, R, placed at the top of each retort, draws into it by a funnel-shaped opening all vapours and powder emitted from the retorts whilst they are being charged, and the draught of which, whenever isolated from the oxidising chamber, is sufficient to draw the products through a series of chambers not shown in the drawing, having cloth screens as usual to retain the oxide of zinc. The ventilation of both the draught pipes, Q and R, is effected by means of the waste heat of the furnace.

The same inventor combines the principle of the reverberatory furnace in the distillation of zinc for the purpose of making zinc white. In this arrangement he so disposes the retorts that the flame from the coal fire circulates round them, and then passes into a chamber over the dome inclosing the retort, where pipes may be laid for raising the temperature of the air which is forced into the space surrounding the mouths of the retorts to oxidise the zinc vapours. The oxide so produced is conducted to receiving chambers in a manner somewhat similar to the two methods already described.

There are several patented modifications of this manufacture, the chief differences being merely in details of mechanical arrangement. Geyelin uses steam instead of air. A jet of steam is admitted at the back of the retort, and in its passage over the molten metal is decomposed, oxide of zinc being formed and hydrogen, which escapes at the mouth and burns in the air. By this method a more dense product might be reasonably expected; but the author has not been able to ascertain if such is the fact.

When ground in oil as a paint, zinc white is frequently adulterated to a great extent, the same materials being used as in the sophistication of white lead, namely, sulphate of baryta, sulphate of lime, and carbonate of lime. They may be discovered by testing in the way described under *White Lead*. After separating the pigment from the vehicle, the powder may be treated with dilute sulphuric acid; the zinc oxide will alone dissolve; carbonate of lime will be converted into insoluble sulphate of lime, its presence being indicated by effervescence. If it is desired to know whether the adulterant is baryta or lime, the white powder remaining after treatment with acid should be washed by decantation, then thrown on a filter, and again washed with hot water. If the powder is now boiled for some time with a strong solution of carbonate of soda, the sulphate of lime becomes converted into the carbonate of that metal, whilst the barium sulphate is scarcely affected. Again, the precipitate must be well washed until quite free from adhering soda salt. It may be then treated on the filter with small quantities of dilute hydrochloric acid. If there is effervescence, it is a sign that lime was present. The liquid parting through the filter should be collected, neutralized with ammonia, and treated with ammonium oxalate. An abundant white precipitate confirms the presence of lime. A white residue on the filter, insoluble in the dilute acid, is barium sulphate. As much as 75 per cent. of sulphate of baryta has been found in paint sold as zinc white.

Griffith's New Zinc White.—There has just appeared in the market a new zinc white, which is almost equal in body to the best white lead, and quite surpasses ordinary samples. It works freely, and mixes well with oil without any tendency to drag. Having for its basis a sulphide of zinc, it is not affected by foul gases, and in all the experiments to which the author has subjected it, does not affect other pigments mixed with it. It would be very desirable to prepare this body for artists' use, as ordinary zinc oxide lacks covering power and does not work well under the brush. It would seem that this new pigment possesses all the good qualities of white lead without any of its defects.

The process of manufacture, as far as is yet known, is as follows:—A solution of zinc sulphate or chloride is precipitated by a soluble alkaline sulphide, which is preferably sufficiently alkaline to

precipitate magnesium oxide from a solution of a magnesium salt which is originally mixed with the zinc salt. But if the alkaline sulphide be too alkaline, there is fear of sodium zincate being formed. The precipitates are dried and heated to a suitable temperature in a reverberatory furnace, and suddenly cooled. Careful grinding is now all that is necessary to prepare it for the market. The presence of magnesia seems to give the pigment that soft quality so much sought for in white lead.

Baryta White.—Sulphate of barium, both natural and artificial, is used as a pigment, but has little body. This defect, however, does not prevent its being used in distemper painting, for which it is eminently fitted. It is chiefly employed, as has been said, in adulterating the whites of lead and zinc. The cheaper product found in the market is native heavy spar, an abundant mineral, ground to a fine powder. It has not such a good colour as the same body produced by artificial means, and does not, accordingly, command such a high price. Moreover, the artificial product is in a finer state of division, as it is produced by precipitation and not by mechanical grinding. In France it is manufactured on a large scale, and is sold under the name of *blanc fixe*. M. Kuhlman, in his extensive alkali works at Lille, manufactures this pigment, utilizing for this purpose the residue from the chlorine stills. He conducts his process as follows:—An intimate mixture of ground heavy spar and bituminous coal is thrown upon the hot hearth of a reverberatory furnace, arranged similarly to that used in the manufacture of soda. This furnace is divided into two compartments by a low wall. The above mixture is placed in that compartment furthest removed from the source of heat. Here it is mixed to the consistency of a thin paste with the still liquor, previously neutralized by chalk, or, better, by native barium carbonate, known as *Witherite*. The greater part of the water is driven off by the heat. When the mass becomes sufficiently thick, it is raked over the partition wall into the hotter portion of the furnace with suitable tools. Here it is calcined for about an hour, carbonic oxide being evolved, which burns on the surface of the mass with a greenish flame, owing to the volatilization of a small portion of the baryta. When the calcination is complete, a point learned by experience, the semi-fluid is withdrawn from the furnace exactly in the same manner as in the manufacture of black ash. It solidifies to a black mass, which contains chloride of barium, a small quantity of hyposulphite of barium, together with sulphides of manganese and iron, and the residue of the bituminous coal. After a few days of exposure to the air, this mass becomes disintegrated (the barium hyposulphite becomes oxidised to the state of sulphate), and is ready for lixiviation. This part of the process is carried on in vats similar to those used in the manufacture of soda. If the materials have been mixed in right quantities, the resulting liquor is an almost pure solution of chloride of barium, marking 24° or 25° Béaume. If it should contain any sulphide of barium (which is easily ascertained by treating a small portion with acetate of lead solution, which will give a black precipitate should any be present), the addition of a small quantity of chloride of manganese will decompose it, forming chloride of barium and sulphide of manganese. Should there be chloride of manganese in solution, sulphide of barium may be used to effect its decomposition with the same result. The clear liquid is drained off from the sediment into vessels for the precipitation of the sulphate of barium. For this purpose dilute sulphuric acid is used, being added until there is no further precipitation. The solid powder soon settles, and the fluid, which consists of weak hydrochloric acid, may be siphoned off from the sed ment. A few washings with pure water remove all traces of acid. It is then drained on cloth filters, in which process it is found convenient to have recourse to pressure. It is sent to the market either as a paste or as a dry powder. The chemical reaction brought about in the furnace may be represented by the equation—

$$BaSO_4 + MnCl_2 + 4C = BaCl_2 + MnS + 4CO.$$

The loss of sulphate of baryta seems to be very small, seldom amounting to more than 5 per cent. M. Kuhlman produces in his works about 2000 kilos. of this pigment per diem.

Whiting, Spanish White.—These whites are prepared either by grinding native chalk or by precipitating carbonate of lime from a soluble salt of lime by carbonate of soda. They are of no use in oil painting, but are used largely in distemper.

There are a variety of earthy whites, which present no advantages over carbonate of lime, found in the market. Whites of cadmium, tin, mercury, arsenic, antimony, and bismuth have been proposed as pigments. They possess no advantages over white lead, as they are all injured by bad gases; moreover they have little body, less even than zinc white, and are bad driers.

Red Pigments.—*Vermilion, Cinnabar, Sulphide of Mercury.*—This pigment is identical in chemical composition with black sulphide of mercury. To obtain it of a fine colour many precautions are required, which experience alone teaches. There are two methods in vogue, both producing excellent results, but differing essentially in their nature. The Dutch, or dry way, will first occupy our attention. Vermilion is produced by this method, by subliming the black sulphide at a high temperature. The *modus operandi* is as follows:—Mercury and sulphur in the proportion of about 88 parts of the former to 22 of the latter are well mixed together, until the whole becomes converted into a homogeneous black powder. This sulphide is known as Ethiops. In furnaces specially adapted for the purpose of sublimation, large pots made of sand and clay well luted are so arranged that the fire may play over about two-thirds of their height. These are provided with well-fitting covers of polished iron. The operation is begun by raising the pots to a dark red heat; the ethiops, which is usually kept in jars of about a pint capacity,

is then thrown in; three jars full is usually enough for the first charge. The flame of burning sulphur rises to a height of 4 or 5 feet above the top of the pot. As this subsides the iron cover is adjusted, and the mass is stirred from time to time with an iron rod which passes through a hole in the cover. Every four or five hours more of the æthiops is added, and the sublimation is continued for thirty-six hours. The proper temperature is indicated by the height of the flame above the edge of the pot when the lid is raised. This should never exceed 4 or 5 inches. At the end of the period above mentioned, the pots are allowed to cool, are then removed from the furnace, and broken. The vermilion, which forms a thick coating chiefly on the sides of the upper part, is then removed, ground in a mill, levigated, and dried. The finer the state of comminution, the more brilliant is the product. No little experience is required in the management of the temperature in the furnaces, as the depth of tone of the pigment seems to depend in a great measure on the regularity with which the sublimation is kept up.

In Idria the process is somewhat modified. The ethiops is prepared by placing 8 lbs. of sulphur and 42 of mercury in barrels, which are made to revolve on their axes until the combination of the two bodies is effected. This usually requires three or four hours. The sublimation is carried on in iron cylinders heated to dull redness. When the charge is first thrown in, tight-fitting iron covers are placed on these cylinders until all crackling ceases. These are then removed, and replaced by earthenware caps connected with tubes to receivers. The temperature is raised and the sulphide sublimed. The cinnabar is found caked in the covers, while some is carried along with uncombined sulphur into the tubes and receivers. This is again returned with fresh ethiops to the cylinders to be resublimed. After finely grinding in water, the product is boiled with caustic soda or potash to remove free sulphur, and subsequently washed with hot and then cold water.

The wet method of procuring this body, sometimes called the Chinese method (because it is supposed to be the method by which the beautiful pigment termed Chinese vermilion is produced), is carried out in one of the following ways:—68 parts of sublimed sulphur moistened with a solution of caustic potash are ground together in a mortar with 300 parts of mercury. The magma, when perfectly homogeneous, is then mixed with a solution of 160 parts of caustic potash in an equal weight of water. The mixture is then heated on a sand bath with constant stirring, fresh water being added to make up for that driven off in evaporation. After a time, arrived at by experience, water ceases to be added, and heat is applied with great care. The substance becomes gelatinous and red, and at a certain moment it attains its most brilliant intensity. This point has to be carefully watched, for a few seconds on one side or the other materially interferes with the beauty of the pigment. When the desired result has been arrived at, the source of heat is withdrawn. The vermilion is then washed with a solution of caustic soda, and afterwards with water. The temperature at which this operation is carried on is a very important matter. It should not exceed 50° C.

The foregoing is the method recommended by Kirchoff; it is known as the Brunner process:—An ethiops is made by mixing intimately 300 grams. of mercury with 114 grams. of sulphur. In small portions at a time is added to this a solution of caustic potash, containing 75 grams. of the alkali to 450 grams. of water. Vessels of porcelain, earthenware, or cast iron are made for heating the mixture. This is performed in a sand bath, care being taken that the temperature never exceeds 50° C. Water is added to make up for the loss by evaporation. After seven or eight hours the black ethiops will have acquired a reddish hue, which soon turns to the characteristic scarlet of vermilion. At this point the vessel is removed from the sand bath. After digestion with warm water for some time, the pigment is well washed by decantation, and separated from uncombined mercury.

Jacquelin's process does not differ essentially from the two processes described, but the proportions of ingredients are not the same. He recommends that 90 grams. of mercury and 30 of sulphur should be mixed with a solution composed of 20 grams. of potash and 30 of water, and this mixture heated for an hour at a temperature of 80° C. The resulting vermilion is washed and dried as usual. Manufacturers have tried to brighten their products by subsequent treatment with nitric acid, potash, and hydrochloric acid; it would seem, however, that when pure materials are used, and the temperature well regulated, such treatment is superfluous. The author would especially call the attention of manufacturers of vermilion by the wet method to the preparation of the potassium or sodium sulphide used. The soda and potash of commerce are never pure, and not unfrequently contain considerable quantities of iron and other metals which would injure the vermilion in colour. If the sulphide used is allowed to settle for some days the chief impurities are thrown down, and the clear solutions may be decanted for use. The manufacture of this pigment is carried on by only a few firms in this country, secrecy being maintained; this evidently points to the fact that the manipulative processes are peculiar, as the chemical composition of the pure product is in all cases the same.

Vermilion is frequently adulterated. Among the substances used for this purpose are red oxide and red chromate of lead, colcothar, red ochre, and brick dust. If any of these substances are present, they will remain as a residue when the vermilion is volatilized. The writer of this article lately examined a specimen of vermilion ground in oil for artists' use, which was shown to contain large quantities of red chromate of lead and crimson lake. In most specimens of vermilion free sulphur is found in small quantities. This can be scarcely looked upon as an adulteration; it may be that much of the quality of the colour is dependent on its presence.

Red Lead, Minium.—This pigment is largely used for painting wood and iron; as an artist's colour it

is by all means to be avoided, as it is quickly affected by foul air, and has no permanency. In its preparation much care is required to produce an article brilliant in colour. Litharge produced from pure lead is used, since impurities, such as antimony, iron, or silver, greatly detract from its purity of tint. This is spread upon the sole of a reverberatory furnace, and heated to dull redness, air being admitted over the fire and by the working doors. It is frequently agitated by means of rakes, and fresh surfaces exposed for oxidation. After about forty-eight hours the desired tint is acquired. It is then ground under iron disks and packed for the market. Red lead has no definite chemical composition, but seems to be a mixture of two oxides, litharge or protoxide, and the brown dioxide. Its formula is approximately Pb_3O_4. Nitric acid dissolves out the protoxide and leaves the brown oxide untouched. A variety of red lead is prepared by heating the carbonate in contact with air; it is called *orange mineral.*

Red Chromate of Lead.—This body will be described under chrome yellow.

Antimony Vermilion. — When sulphuretted hydrogen gas is passed into an acid solution of an antimony salt, an orange-coloured precipitate is formed which has been used in various forms as a pigment. If, however, the salt of antimony is heated with hyposulphite of soda, the resulting precipitate has a deep scarlet hue. To obtain a good product, pure chloride of antimony should be used. It can be obtained by dissolving the sulphide of that metal in boiling hydrochloric acid, sulphuretted hydrogen being set free. The resulting solution should be then boiled down until it becomes quite thick; in this operation any arsenic which was present in the crude mineral is driven off as chloride. The residue on cooling solidifies into a mass of a buttery consistency. This should be broken into lumps, and introduced into a retort to which a convenient receiver is adapted. On applying heat the mass melts and distils, the non-volatile impurities remaining in the retort. The distillate crystallizes on cooling. On mixing the distillate with water, a white precipitate is formed which is usually called an oxychloride. On adding a saturated solution of hyposulphite of soda to this mixture the precipitate is quickly dissolved. The temperature of the solution should now be gently raised in a water bath until it reaches about 30° C., when a precipitate will begin to form, at first of an orange colour; as the temperature rises it becomes scarlet. At about 55° C. the vessel should be removed from the water bath. The whole of the antimony will be precipitated, provided a sufficiency of hyposulphite was added in the first instance. The pigment should then be washed, at first with very dilute hydrochloric acid, and afterwards with water. Hyposulphite of lime may advantageously replace the sodium salt; a higher temperature is, however, necessary to bring about the reaction. If prepared with care, this pigment has good colour, and gives pure tints with white. It covers well, and is not affected by light or impure air. It is said to turn brown in course of time.

Kermes Mineral is another sulphide of antimony which has been used as a pigment. When black sulphide of antimony is dissolved by heating it in a solution of carbonate of potash, and the solution is allowed to cool, a red powder is deposited which is called kermes mineral, the chemical composition of which is not definite. It is best to filter off the solution *hot*, and then a very clean red precipitate is formed when the filtered liquid cools.

Red Ochre.—This pigment will be treated of under *Yellow ochres.*

Colcothar, English Rouge.—In the manufacture of Nordhausen sulphuric acid a residue is left in the retorts, which formerly was known under the name of *caput mortuum vitrioli.* It consists of sesquioxide of iron, resulting from the decomposition of the sulphate of iron employed. After grinding and levigation it is ready for the market, and is known as colcothar. It is more carefully prepared by first driving off the water of crystallization from pure sulphate of iron by heat, and then grinding the resulting white substance to powder. On heating this in closed retorts, sulphurous and sulphuric acids are driven off, and the ferric oxide remains behind. Care must be taken not to raise the temperature too high, or the resulting powder will be too brown. It is also prepared by roasting precipitated ferric oxide at a dull red heat. To effect this pure sulphate of iron in solution is treated with carbonate of soda. The resulting precipitate, which is at first of a dingy green colour, becomes brown on exposure to the atmosphere. After washing and drying it is carefully calcined, the temperature being so regulated as to produce a fine tint. This pigment is much used for painting iron. When made up as a paint it is not unfrequently adulterated to a large extent with sulphate of baryta. After getting rid of the oil by the usual methods, this may be easily detected by heating the powder with hydrochloric acid. The sesquioxide of iron will be dissolved, and the barium sulphate will remain as an insoluble white powder.

Lakes. — These pigments consist essentially of alumina, or a mixture of alumina and hydrated ferric oxide, with a vegetable or animal colouring matter. The usual method of proceeding in their preparation is to mix a proper proportion of alum in solution with the aqueous extract of the colouring substance, and then add carbonate of soda. The alumina is precipitated, and carries down with it the colouring principle. When a ferric is used along with the alum, the lakes have a darker hue, resulting from the admixture of the red brown oxide of that metal. The addition of a certain proportion of perchloride of tin has also an effect on the resulting colours. Thus the red colouring principles of the dye-woods of Brazil, Santa Martha, Lima, Sapan, Pernambuco, &c., can be all converted into pigments. Campeachy (logwood) produces purple or violet lakes. Quercitron bark gives a yellow lake. Unfortunately these pigments, although delicate in tint, have no stability, being affected by light. Those, however, produced from the colouring principles of madder are quite permanent.

Madder Lakes.—Madder is the ground root of the *Rubia tinctorum*. It has long been cultivated in the East and in Holland, and latterly most successfully in France, for purposes of dyeing. This plant contains many colouring principles, which have been carefully studied by chemists; in fact, the literature of the subject is voluminous. Madder lakes, however, owe their colour chiefly to one principle, which has been termed *purpurine*. There are many methods of treating madder for the production of lakes, which space will not permit us to discuss in detail. The process, however, devised by M. KHITTEL, following in the steps of PERSOZ, and described at length in the *Technologiste*, are interesting. He takes garancin, produced by treating the madder powder with two-thirds of its weight of concentrated oil of vitriol, and steeps it in a cold solution of sulphate of soda for twelve hours. The most satisfactory proportions are found to be—

Garancin,	1 kilo.
Sulphate of soda,	1 "
Water,	36 litres

After standing it is well washed and pressed, until all traces of the sulphate are removed. A quantity of alum, equal in weight to the garancin originally taken, is dissolved in 10 or 12 times its weight of water, and boiled. It is then removed from the fire, and the purified garancin is introduced. The madder should not be boiled, or the resulting colour will be injured. After about twenty minutes, the greater portion of the colouring matter will have been extracted. The liquid is then filtered from the residue. When it has cooled down to a temperature of about 45° C. subacetate of lead is added in quantity equivalent to that of the alum employed. On stirring the mixture, sulphate of lead is precipitated and rapidly subsides. The clear liquid is then decanted before it has had time to cool. It is then heated for some time to nearly the boiling point, when a purple red lake separates of a beautiful bright tint. The liquor is not yet exhausted, however. It is divided into two equal portions; to one of which is added a solution of carbonate of ammonium until a slight turbidity is caused. The two portions are then mixed and again heated, when a new quantity of lake is thrown down, which, however, is not so bright as the first. Great care must be taken in drying these lakes, as with all madder lakes. An elevated temperature destroys their brilliancy.

M. SACE obtains fine madder lakes by using the pasty alcoholic extract of madder. He mixes 50 grams. of water with 100 grams. of the extract, and allows the mixture to macerate for twenty-four hours. More water is then added, and the solution is separated from the solid residue by passing it through a silk sieve. A boiling solution of alum, containing 100 grams. of the salt to 1 litre of water, is gradually added with constant stirring. This lake has a deep red tint. By substituting sulphate of sesquioxide of iron for the alum, a deep violet lake is formed.

M. KOPP treats the powdered root with a solution of sulphurous acid, and allows it to macerate. The hot filtered liquid is then treated with acetate or hyposulphite of aluminium, or with alum neutralized with carbonate of soda. Four kinds of lakes are successively deposited; the first is bright dark red, the second is of the same hue but lighter, the third is a pure pink, and the fourth a yellowish pink.

Madder lakes are frequently adulterated with lakes formed from other cheaper colouring matters, and the violet lakes are sometimes found to contain Prussian blue. M. CHATEAU has devoted some attention to these adulterations. We quote his methods of detection as given in MALEPEYRE'S treatise "On the Manufacture of Colours:"—

Red and Pink Lakes.—"These lakes do not colour either hot or cold water. They colour alcohol and ether very slightly, and only after a certain length of time. By calcination they leave a white residue of alumina.

"*Santaline.*—If the lake be dark it may contain santaline, which is detected by the *orange-red* colour acquired by the ether digested with the suspected lake. Alcohol, under the same circumstances, would be coloured *red*.

"If the lake be of a pink hue, it may be falsified with lakes of Brazil wood or cochineal. But as madder lakes, and generally all lakes, are insoluble in water, ether, or alcohol, their colouring substance should be insulated, and I propose the following method:—Every lake with alumina for base is soluble in hydrochloric acid, or in acetic acid to which a few drops of the former acid have been added, or in a solution of protochloride of tin. After the lake is dissolved, ether is added to the solution, and the whole is shaken. All the colouring matter is dissolved in the ether, which will acquire different colorations, according to the lakes introduced.

"*Lakes of Brazil wood—First Process.*—Let us suppose that a madder lake is adulterated with the lakes of Pernambuco, Japan, or Brazil wood, the colouring matter will be rendered soluble in ether by the process indicated above, and the ether will be coloured a gold-yellow.

"*Venice Lake, ball shape—Second Process.*—A madder lake adulterated by Venice lake, ball shape (one of the finest lakes of Brazil wood), will disengage ammonia if it be heated in a test tube with a solution of potassa. Under the same treatment a pure madder lake does not produce ammonia.

"*Brazil Lake—Third Process.*—A madder lake, falsified with the lakes of Brazil wood, will be generally recognized by its effervescence with the acids, and its blue coloration by iodine. These reactions are due to the presence of chalk and starch, which are used for thickening the lakes made with Brazil wood.

"*Carmine Lake.*—Another adulteration of madder lakes is that with the so-called carmine lakes of an inferior quality. This fraud is easily detected.

"Water *is not coloured* with madder, while it *is coloured* with carmine lake. The coloration is immediate, and becomes more intense by heating. This aqueous solution of carmine lake becomes *violet* by soluble alkalies, and gives a *violet* precipitate with

lime water, chloride of tin, sulphate of copper, acetate of lead, and sulphate of zinc.

"All that has been said about red and pink lakes may be applied to the *madder carmine*.

"*Violet Lakes.*—The violet madder lakes, after calcination, leave an ash of oxide of iron, which, being dissolved in hydrochloric acid, produces an abundant precipitate of Prussian blue by the addition of ferrocyanide of potassium.

"These lakes, under the action of hydrochloric acid, turn a dirty *orange-yellow* colour.

"*Campeachy Lakes.*—1. If adulterated with Campeachy lakes, the addition of hydrochloric acid will produce a *crimson-red* coloration. After calcination the ash will be nankin-yellow or white, whether the Campeachy lake is partly or entirely substituted for that of madder.

"2. After having extracted the colouring matter in the afore-mentioned manner, the ether is coloured a *gold-yellow*, and will give the Campeachy reaction, if that substance be present.

"*Alkanet.*—1. The madder lakes, falsified by alkanet lakes, are easily recognized. The lake is dissolved in acetic acid, and bisulphide of carbon is added, which after shaking is coloured an intense violet red if alkanet be present. This reaction is characteristic of that substance.

"2. A madder lake adulterated by alkanet disengages violet fumes when heated. Moreover, such a lake is coloured blue by alkalies, baryta, and lime.

"3. After solution of the adulterated lake in acetic acid, and separation of the colouring matter in ether, this is evaporated, and the residue is treated by alcohol, which dissolves the colouring principle of alkanet. This alcoholic solution gives a blue precipitate with lead subacetate or acetate, if it contains anchusine, the colouring matter of alkanet.

"*Orchil.*—Orchil lake is dissolved in hydrochloric acid, which becomes red. Ether, shaken with solution, does not dissolve a trace of the colouring matter. The same reaction takes place with bisulphide of carbon.

"*Prussian Blue.*—Prussian blue, added to a violet madder lake for the purpose of deepening the hue, is recognized by the addition of hydrochloric acid, which changes the violet of the lake to a green. Hypochlorites, and especially hypochlorous acid, turn the violet to a blue.

"*Black Lakes.*—By calcination these lakes give an ash of oxide of iron. Hydrochloric acid changes them by degrees into a dirty orange. They turn a brown, rusty colour by the action of protochloride of tin.

"*Charcoal and Lamp Black.*—These lakes being of a fine black colour, it is possible to falsify them with finely-ground charcoal or lamp black. This fraud will be detected by boiling the sample with hydrochloric acid, which will dissolve the lake, and will leave the charcoal or lamp black as a residue.

"*Black Campeachy Lakes.*—Black madder lakes may be mistaken for those of Campeachy. The latter will redden strongly by the action of hydrochloric acid and of the protochloride of tin. In the first case the red portions will stain paper a cherry-red colour; in the second case, a more or less violet red.

"*Lake with Cochineal Basis.*—In order to distinguish a black madder lake from one with cochineal basis, an addition of chloride of tin will turn the cochineal lake a cherry-red, and white paper will be stained. The madder lake presents no such reaction.

"*Black Sumach Lake, &c.*—While the black madder lakes are of a pure colour, those manufactured from galls, sumach, and other astringent substances, are olive-black. I do not believe that the latter can be mixed with the former, on account of the olive hue. Moreover, the adulteration must be considerable in order to be profitable."

Besides the vegetable colouring matters already named which serve to produce lakes, there are many others. The boughs of buckthorn and the berries of the elder give violet, red, chocolate, and brown decoctions, the colouring matters of which can be combined with alumina, oxide of tin, magnesia, oxide of zinc, and oxide of antimony. They are, however, of little value to the artist on account of their want of stability.

Carmine or Crimson Lake.—This lake, so exquisite in tint, is unfortunately affected by light. It is prepared from the colouring matter of the cochineal insect (*Coccus cacti*). Twenty parts of powdered cochineal are boiled with 400 parts of water and 10 parts of cream of tartar. After filtration, a solution of 300 parts of alum with a small quantity of protochloride of tin is added to the decoction. The precipitate first formed is exceedingly brilliant; the liquid still, however, contains the greater part of the colouring matter. To effect its precipitation a solution of carbonate of soda is cautiously added, when the alumina becomes wholly precipitated along with the colouring matter.

Carmine.—This brilliant but fugitive pigment is also prepared from the cochineal insect by different methods, most of which are kept secret. It is not a lake in the ordinary acceptation of the word, as it contains no base equivalent to alumina. The phosphate and carbonate of lime, which are found in small quantities, are derived from the insect itself. It seems to be essentially a mixture of fatty matters with the acid used for precipitation and the colouring matter of the insect. DE LA RUE, who has carefully investigated the subject, terms this colouring matter *carminic acid*, and assigns to it the formula, $C_{14}H_{14}O_8$. The following are a few of the methods made public by which this pigment may be produced. For other processes and the chemistry of carmine, see the article on COCHINEAL in vol. I. of this Dictionary.

The Old German Recipe.—Take 580 parts of clear river water, and boil; add 16 parts of powdered cochineal, stir well and allow to boil for six minutes; then add 1 part of ground alum, and boil for three minutes more. Remove from the fire, and filter into porcelain vessels. Leave to settle for three days, and separate the liquid from the precipitated carmine. On standing for a further length of time,

a second inferior deposit is obtained. The liquid, which still contains much colouring matter, may be used for the preparation of carmine lake.

Carmine with Tartar.—To 8 lbs. of boiling water are added 8 ozs. of cochineal, and after a little time, half an ounce of cream of tartar. After boiling for eight minutes, three-quarters of an ounce of alum are added, and the boiling continued for a few minutes. The rest of the process is conducted as before.

The Alxon or Langlois Process.—30 pints of boiling water are mixed with 1 lb. of cochineal; and after a time, a solution of 6 drachms of carbonate of soda to 1 lb. of water is added. After boiling for an hour, the decoction is removed from the fire, and 6 drachms of powdered alum are added, the liquid being agitated with a brush. The liquid, after resting for twenty minutes, is carefully decanted, and then is added, with constant agitation, a solution containing the whites of two eggs beaten up with half a pound of water. After reheating for some time the liquid is allowed to cool, when the carmine is deposited.

Process of Madame Cenette.—To 6 parts of boiling river water are added 2 lbs. of cochineal, and the boiling continued for two hours; then are added 3 ozs. of saltpetre and 4 ozs. of salt of sorrel. After ten minutes the vessel is removed from the fire, and the liquid is allowed to settle for four hours. The clear liquid is siphoned off into shallow plates, and left for three weeks to deposit the carmine. A mouldy mass is formed on the surface; this is dexterously removed by a piece of whalebone, care being taken not to break it. The supernatant liquid is then siphoned off, and the carmine dried in the shade.

Carmine of China.—The cochineal solution is made as in other processes, with the addition of Roman alum. This solution is then added, drop by drop, to the clear liquid, until all the carmine is precipitated.

Ordinary Carmine.—60 pints of water, 1 lb. of cochineal in powder, and 3½ drachms of carbonate of potash are boiled together. The vessel is removed from the fire and placed in a convenient position for decantation, 3 drachms of powdered alum are added, and the liquid soon becomes clear. It is then decanted, and again placed on the fire. Then a solution of 3 drachms of fish glue in a large quantity of water is added. As soon as ebullition sets in the vessel is removed, and the liquid strongly agitated. Carmine is precipitated and collected in the usual manner.

This pigment is frequently adulterated. It should be quite soluble in ammonia. Any residue left, therefore, on digesting a sample with this reagent, may be looked upon as foreign matter added for purposes of sophistication.

Madder Carmine.—M. Bourgeois discovered, early in the present century, a preparation from madder which is said to possess all the permanent qualities of the madder lakes, but to exceed them in delicacy and depth of tint. His process has been kept secret. M. Lefort, however, in his "Chimie des Coleurs" gives a method of preparing a brilliant madder carmine. He first causes the root, which should be of the best quality, to enter into fermentation by placing it in a damp place. When the saccharine matter is thus destroyed and acid fermentation has set in, he treats the disintegrated root with sulphuric acid diluted to 55° Beaumé. Great care must be taken at this stage of the operation that the temperature should not rise too high. For this reason he makes the addition of acid in a leaden vessel, surrounded with cold water. After standing for three or four hours the paste is treated with cold water, and the residue removed from the solution by filtration through a bed of broken glass. The filtrate is received in a large quantity of pure water. The carmine is soon deposited from this solution, and can be collected and dried in the usual manner.

Rose Pink.—This common pigment, largely used in paper staining and distemper, consists merely of chalk coloured with solution obtained from dye-woods. It has no permanency.

There are many other red pigments, both organic and inorganic, known to chemists; but they are mostly curiosities of the laboratory. Scarlet iodide of mercury merits mention on account of its surpassing brilliancy. It is produced when a solution of potassic iodide is mixed with a mercuric salt, the perchloride being preferable. It is soluble in excess of either of the reagents, and it therefore requires some care in exactly hitting the medium. Bad gases quickly affect it, and it loses its brilliancy by exposure to light. It is, however, still used as a pigment by artists; it must never be allowed to come into contact with metallic iron, as it would be decomposed; it should never be mixed with other pigments, and when employed should be mixed with such a medium as will thoroughly protect it from the air. Cobalt furnishes rose pinks of considerable intensity; but as they are thrown into the shade by madder colours, they find no place on the artist's palette. Ferrate of barium, chromate of silver, perchloride of chromium, hyposulph-arsenite of manganese, persulpho-molybdate of calcium and barium, terchromate of thallium, &c., have all been suggested as pigments; but they are mostly inadmissible.

Yellow Colours.—*Yellow, Orange, Red, and Brown Ochres.*—These pigments are clays, which owe their colour chiefly to sesquioxide of iron existing in a greater or less state of hydration. They are found abundantly in nature, and merely require floating to remove grit, &c., and drying to prepare them for artists' use. The finer their state of comminution, the more fitted they are for the palette. They have no definite chemical composition. The well-known yellow found at Saint-Georges-sur-la-Prés has the following composition:—

Clay,	69·5 per cent.
Oxide of iron,	23·5 "
Water,	7·0 "

Under this head may be classed the *Terra di Sienna*, a pigment most useful to the artist, both in its *raw* state and also when calcined or *burnt*. *Venice* and *Antwerp reds*, and a variety of tinted earths found in different localities, belong to this class. By subject-

ing the yellow varieties to a greater or less degree of calcination, a great variety of hues may be obtained. With regard to permanency, the ochres leave nothing to be desired. The brown varieties frequently contain manganese. An artificial ochre known as *orient yellow*, of a fine pure tint, is spoken of very highly.

Mars Yellow, Orange, Brown, and Red.—These pigments consist of sesquioxide of iron, containing more or less water of hydration. The method of preparing them is kept secret. They are not unfrequently adulterated with chromate of lead, orpiment, and sulphate of lime. When treated with a solution of sulphuretted hydrogen, no blackening should ensue. A spurious imitation containing sulphate of lime is obtained by treating ferrous sulphate with milk of lime, and exposing the resulting precipitate to the action of the air. The hydrated monoxide of iron thus becomes oxidised to ferric oxide,and the sulphate of lime formed remains intimately mixed with it.

Iron Yellow—Oxalate of Iron.—This pigment is produced when a boiling saturated solution of oxalate of ammonium is added to a hot solution of ferrous sulphate. It can scarcely be recommended. With Prussian blue it does not form greens, as a mutual decomposition takes place when the two bodies are brought together. It is decomposed by lime and other alkaline bodies.

Naples Yellow.—The old Naples yellow is an antimoniate of lead produced by different processes. Many recipes are given for its production. The three following give good tints:—

1. Tartar emetic	1 part.
Nitrate of lead	2 parts.
Chloride of sodium	4 "

This mixture is heated to fusion for two hours in a crucible. It is then powdered, and the chloride of sodium carefully washed out with water.

2. Two parts of pulverized type metal (an alloy of equal parts of lead and antimony) are fused with 4 parts of nitre and 6 parts of chloride of sodium. The product is washed free from soluble matter.

3. Twelve parts of white lead, 3 parts of antimoniate of potash, 1 part of sal-ammoniac, and 1 part of alum, are intimately mixed and kept at a red heat in a crucible for three hours. The soluble salts are removed by washing.

Brunner, who specially studied this compound, prefers the first method of preparation. As a pigment it possesses a good body, but is quickly affected by foul air. It is also decomposed by contact with iron; hence a palette knife of wood or ivory must be used in collecting it. The pigments now usually sold as Naples yellow are mixtures of white lead and chromate of lead, or zinc, or ochre. White lead and dark cadmium yellow, mixed in proper proportions, imitate the shade of colour fairly well. Indeed, this mixture is much less objectionable for artistic purposes than the real yellow. (See Antimony.)

Cadmium Yellows.—These pigments are compounds of sulphur and cadmium. They may be prepared either by passing a stream of sulphuretted hydrogen through a solution of a cadmium salt, or by heating the oxide of the metal, or the metal itself, with sublimed sulphur. When made with care from pure cadmium salts, and when free from uncombined sulphur, they are eminently good pigments. They are brilliant in tone and stable. A cadmium red has also been obtained possessing all the virtues of the yellow pigments. Cheap cadmiums obtained from abroad are almost invariably adulterated, or prepared without due care, and are therefore very objectionable for artistic purposes.

Indian Yellow is an organic substance of indefinite composition; as a pigment, it is not trustworthy.

Chrome Yellows.—Under this head may be included the chromates of lead, zinc, barium, strontium, and calcium. They are for the most part prepared by double decomposition, from the admixture of a soluble chromate with a salt of the metal. For this purpose the chromate or dichromate of potassium is usually employed, but under certain circumstances the corresponding sodium salt, and even the chromate of lime, is used. The manufacture of these chromates has undergone considerable modification during the last few years. New and more economical methods have been substituted for the older plans of preparation, as the demand and consumption have increased. The former plan of producing the yellow chromate of potassium consisted in mixing finely-powdered chrome ironstone with nitre, and fusing the two bodies together on the bed of a reverberatory furnace. The mass was subsequently lixiviated; the filtered yellow solution was then boiled down rapidly, so as to deposit the salt as a granular crystalline powder. After draining these crystals were redissolved, and the solution slowly evaporated so as to obtain larger crystals; or a quantity of mineral acid was added to this neutral chromate, until it became converted into acid chromate thus:—

$$2(K_2CrO_4) + 2(HNO_3) = 2(KNO_3) + H_2O + K_2Cr_2O_7.$$

The red acid chromate was then separated from the nitrate or other salt formed simultaneously by crystallization. It was found that a portion of the nitre might be dispensed with, and pearl ash (carbonate of potash) substituted; or that by admitting air into the reverberatory furnace, the oxidation might be carried out without the aid of nitre. Stromeyer suggested the admixture of lime with the ore and pearl ash. This addition makes the mixture thick, so that it may be easily turned, and thus every portion may be exposed to the oxidising influence of the air. Before this suggestion was adopted, much mechanical difficulty was experienced in decomposing the whole of the chrome ore, as it sank to the bottom of the thin alkaline fluid, and thus escaped oxidation. Watt still further economized the manufacture by substituting the cheaper sulphates of sodium or potassium for the carbonates. Tilghman uses felspar as the source of alkali. He mixes 4 parts of that mineral in powder with an equal weight of lime and 1 part of the chrome ironstone, and calcines the mixture in a reverberatory furnace. The subsequent operations for producing the crystalline salt are similar in all these methods to that already described, differing only in mechanical details. The process devised by Booth, of Phila-

delphia, consists of two operations. The powdered ore is first agitated with coke or charcoal; the iron is thus reduced to the metallic state, and may be dissolved out from the mass by dilute sulphuric acid. The sulphate of iron thus formed is evaporated and crystallized. The chromic oxide is then fused with alkali and nitre to produce the chromate. Oxygen is thus economized, as there is no loss, as in the other methods, in converting the monoxide into the sesquioxide of iron; the by-product of green vitriol also defrays some of the expense of working. Jacquelain decomposes the chrome ironstone by chalk, to form the acid chromate of calcium. To this end he mixes the finely ground ore with the powdered chalk in proper proportions, and spreads it in a layer of about 2 inches deep on the floor of a reverberatory furnace. It is then heated for nine to ten hours to bright redness, being frequently turned over during the calcination. The greenish-yellow mass produced, which consists for the most part of ferric oxide and neutral chromate of calcium, is ground to a fine powder. This powder is mixed with water, and sulphuric acid is added until a slight acid reaction is perceptible. The neutral chromate of calcium is thus converted into the acid salt, which remains in solution. The small quantity of sulphate of iron formed at the same time is decomposed by stirring up the liquid with fresh carbonate of lime, which precipitates the iron. To prepare the potassium dichromate from the solution, it is only necessary to treat it with a proper quantity of carbonate of potassium, when by double decomposition carbonate of calcium is formed and precipitated, while the potassium dichromate remains in solution. For the preparation of pigments this last operation is unnecessary, as the calcium dichromate may be used directly.

Chromates of Lead.—The neutral chromate of lead, of a light yellow colour, is easily produced by mixing together a dilute solution of nitrate or acetate of lead (by preference, nitrate) and one of chromate of potassium. The reaction may be thus represented:—

$$K_2CrO_4 + Pb(NO_3)_2 = 2KNO_3 + PbCrO_4.$$

If the solutions are too concentrated, an orange precipitate is produced. It may be also prepared from sulphate of lead by treating that powder with chromate of potash. Liebig proposed to utilize the sulphate of lead, obtained as a by-product in several industries, for the manufacture of this pigment. In practice, however, it is found that the whole of the sulphate is not decomposed, nor does the product cover so well as that produced by precipitation.

Basic chromate of lead, or orange chrome, when quite free from the neutral salt, may be produced by digesting the neutral chromate in caustic alkalies. It has the formula—$PbO.PbCrO_4$. According to the mode in which it is prepared it assumes various hues, from light orange to deep scarlet. One method of preparing it consists in boiling the neutral chromate with caustic lime. A portion of the chromic acid thus passes to the lime and remains in solution. The precipitate has now acquired an orange tone, which may be deepened by cautious heating after it has been well washed and dried. Or again, a solution of a lead salt may be precipitated by chromate of potassium containing free alkali. By varying the proportions of soda or potash, added for this purpose, different tones of orange may be produced. When a great excess of alkali is used, the brownish orange precipitate first formed begins soon to alter its character on standing undisturbed. Scarlet patches begin to form in the precipitate, which gradually extend through the whole mass. It thus passes from the amorphous into the crystalline form. The finest-coloured product is obtained by throwing the neutral chromate of lead, by small quantities at a time, into a crucible filled with melted nitre. The basic chromate thus formed is of a deep cinnabar scarlet. It sinks to the bottom of the crucible. The liquid above it may then be poured off and used for subsequent operations. The sediment should be well washed. A brilliant scarlet may be also produced by treating white lead with chromate of potassium. The scarlet modifications of this chromate have little body, on account of their crystalline nature. They are known as Persian reds.

Chromates of lead are adulterated frequently with chromates of lime, baryta, and sulphate of lead. To detect these sophistications requires some practical acquaintance with analysis. The very objectionable pigment which goes by the name of *Cologne yellow* is a mixture of sulphate of lime, sulphate of lead, and chromate of lead. The two first bodies form about 75 per cent. of the whole. As pigments the chromates of lead are objectionable on the same grounds as other pigments having lead for a basis, they are quickly attacked by foul gases. They also have a tendency to turn green by reduction of the chromic acid, and this is effected by organic substances with which they are mixed, when used as pigments.

Chromate of Lime.—This pigment is little used in oil painting. It may be prepared by mixing together chloride of calcium and chromate of potassium, and precipitating the mixed solutions with ammonia. After draining away the liquids the precipitate may be heated to about 200° C., when it loses water and becomes very much less soluble in that menstruum. The soluble salt may be then washed out. As a pigment it cannot be recommended for artistic purposes.

Chromate of Baryta may be prepared by adding chromate of potash to nitrate or chloride of barium. It is nearly insoluble in water, and has a fine lemon-yellow tint. It has been said that it becomes greenish on exposure to light; this is not the experience of the author with the pure compound. It is known in the arts by the name of "lemon yellow."

Chromate of Zinc.—This beautiful and stable pigment is prepared by treating a hot solution of sulphate of zinc with chromate of potash. The zinc solution must be perfectly neutralized with carbonate of soda, or the precipitate produced will be of pasty consistency, and of a faint straw-yellow hue, in place of the pulverulent fine yellow chromate. This pig-

ment may be safely recommended to the artist, when prepared from pure materials.

Other yellow chromates have been proposed as pigments, as, for instance, the chromates of thallium and cadmium; but they have many disqualifications. Strontium chromate, which may be prepared in a similar method to the barium chromate, has no advantages over the latter body.

Iodide of Lead.—This compound is produced when a soluble lead salt is precipitated with iodide of potassium. Besides being soluble in hot water, it is quickly affected by light.

Massicot.—This is a monoxide of lead, varying in colour from a pale straw to an orange-yellow tint. It may be prepared by gently calcining white lead in a reverberatory furnace. It is seldom used by artists.

Turner Yellow, *Carsel Yellow*, *Montpellier Yellow*, *Verona Yellow.*—These yellows seem to be oxychlorides of lead, varying in composition. They are produced when red lead or litharge is heated with common salt or sal-ammoniac. Besides having the disadvantages of all pigments with a lead basis, they are quickly affected by light. A variety known as mineral straw yellow is more durable than the preceding.

Orpiment.—This mineral, which is the trisulphide of arsenic, when ground to a fine powder is sometimes used as a pigment. It can be procured artificially by subliming a mixture of 1 part of flowers of sulphur and 2 parts of arsenious acid. It is wanting in durability, and is poisonous. When a stream of sulphuretted hydrogen gas is passed through a solution of arsenious acid, the yellow precipitate formed has the same chemical composition as orpiment, and has the same disadvantages as that body. It is known as *King's yellow*, and invariably contains arsenious acid. There is some doubt as to whether pure arsenious sulphide is poisonous.

Mineral or *Arsenic yellow* is a pigment containing both arsenic and lead. It may be produced by fusing together litharge and arsenious acid, and reducing the resulting mass to powder. For the reasons cited above, it is not to be recommended as an artist's colour.

Aureolin.—Much has been said in praise of this pigment, which is the nitrite of potassium and cobalt. It is a pure transparent yellow, of great tinctorial power. It is said to be quite stable, although its chemical composition would suggest doubt. It can be prepared by precipitating a salt of cobalt by carbonate of soda, washing the precipitate, and dissolving in excess of acetic acid: this solution is treated with a slight excess of nitrite of potassium. The precipitate takes some time to form, and invariably contains the whole of the cobalt of the original solution, in so much that it is used as a quantitative separation of cobalt in analysis. The chemical composition of this pigment has not been definitely determined. It completely resists the action of a moderately dilute solution of caustic soda, and is therefore suitable for fresco and siliceous painting.

Green Pigments.—*Terra Verte*, *Verona Earth.*—Many localities furnish these earths, which are very useful on the palette. They owe their colouring power to monoxide of iron, which seems to be prevented from absorbing more oxygen from the air by some organic substance, the nature of which has not as yet been well investigated. Besides silicate of alumina, they contain variable quantities of magnesia. In some varieties copper is found, which adds indeed to their brilliancy, but detracts from their durability. They are prepared for use by washing and floating the powdered mineral, so as to remove all gritty matter.

Copper Greens.—There is an immense variety of greens having copper for a basis, all of which, however, are injured by bad gases.

Copper Carbonates.—The most stable of these greens is the native *malachite*, or mountain green. Its composition may be expressed by the formula $Cu_2CO_4 + Aq$. The finest portions of the ore are picked out and ground to a fine powder for use as a pigment. Its crystalline texture militates against its covering power. Damp, and foul gases are fatal to this colour. It is also decomposed by alkaline bodies: it cannot, therefore, be used with safety in fresco, on account of the lime employed in that mode of painting. It can be prepared artificially by precipitating a salt of copper with carbonate of soda.

Green Verditer, *Bremen Green.*—These pigments, which vary much in shade owing to slight differences in their mode of preparation, are hydrated oxides of copper. The first step in their manufacture is the production of a basic chloride of copper. This is effected in several ways: 1, by exposing to the action of the air scrap copper in contact with moist sulphate of potash and common salt; 2, by treating old copper sheathing with dilute sulphuric acid and common salt; 3, or by treating the copper with a solution of chloride obtained by acting upon copper scales (oxide of copper) with hydrochloric acid. In whatever way the basic chloride is formed, it is necessary for success in the production of these pigments that no subchloride should be present, as it would interfere with subsequent reactions. This is insured by exposing the magma to the action of the atmosphere for a long period of time before using it: 100 parts of this basic chloride are then mixed with a concentrated solution of sulphate of copper, containing 7 parts of the salt; to this is added 40 parts of a solution of caustic soda or potash, marking 32° to 36° Beaumé. The precipitate formed is well washed, and carefully dried at a low temperature.

Brunswick Green.—This pigment may be produced by acting upon poor copper ores with hydrochloric acid in contact with air, or by exposing copper turnings moistened with sal-ammoniac. An oxychloride of copper is thus formed, which may be worked off with water and carefully dried. The Brunswick greens found in the trade are, for the most part, mixtures of Prussian blue and chromate of lead or zinc, with a basis of baryta or carbonate of lime. The chromates react on Prussian blue, and this is

shown by the greens turning brownish or "foxey." There are other kinds which contain in place of the chromate a vegetable yellow, probably a preparation of quercitron bark. Some of these latter greens are used in house painting, and retain their colour well. These also soon lose their brilliancy, and become brownish. Brunswick green is never used as a pigment by artists. Messrs. BLUNDELL, SPENCE, & Co., of Hull, have long been noted for their excellence in the manufacture of this paint.

Schweinfurt Green, known also as *Emerald Green*, &c., is an aceto-arsenite of copper. There are several methods of preparing it. LIEBIG directs that 1 part of verdigris be heated with sufficient weak acetic acid to dissolve it: to this 1 part of arsenious acid dissolved in water is added. The precipitate produced is of a dirty green colour. It is dissolved in a fresh portion of acetic acid, and the solution boiled. After some time a brilliant precipitate is formed, which is carefully drained and washed. The colour may be heightened by boiling with a weak solution of potash. Another method consists in mixing to a thick paste with warm water acetate of copper, and then adding a boiling aqueous solution of arsenious acid. Again, a hot saturated solution of 6 parts of sulphate of copper is mixed with another solution prepared by mixing 6 parts of arsenious acid with 8 parts of carbonate of potash. The dirty green precipitate obtained is converted by acetic acid into a fine green. This pigment is highly poisonous. It is chiefly used in paper staining, and seems to stand well.

Much has been written in warning against the use of paper hangings coloured with these arsenical pigments. They are certainly very dangerous when the powder is not firmly fastened with strong size. It is, however, a popular error to suppose that the pigment emits poisonous fumes at ordinary temperatures. It is abraded particles which mix with the dust of the room, and render the air noxious. To test a suspected paper, portions of it should be placed in a retort connected with a receiver surrounded with cold water. Strong hydrochloric acid should be added to the paper, and the distillation carried on until about one-half of the liquid passes over. The distillate may then be examined for arsenic in the usual way; that is, by passing sulphuretted hydrogen gas into the solution, when, if arsenic be present, a bright yellow precipitate will be formed, soluble in sulphide of ammonium, also in a solution of carbonate of ammonia. Care must be taken in this operation not to inhale any fumes that may escape, as the chloride of arsenic formed is an insidious poison. Not only the green colours in wall papers often contain arsenious acid, but some of the bright reds, blues, and purples, likewise contain it in considerable quantity.

Scheele's Green.—This is an arsenite of copper, darker in hue than the one described, and does not contain acetic acid. It is produced by precipitating a solution of sulphate of copper with arsenite of potash. It does not seem to be so durable as Schweinfurt green; it is also poisonous. *Nitis green*, *Vienna green*, *Kirchberger green*, are also arsenites of copper. They are prepared in the same manner as SCHEELE'S green. They are frequently found greatly adulterated. *Green ashes* are prepared by the admixture of arsenite of lime with sulphate of copper. Insoluble sulphate of lime is thus formed along with the arsenite of copper. *Paul Veronese green*, *English green*, *Neuwied green*, *Mineral green*, &c., belong to this class. They are not to be recommended as artist's pigments.

Verdigris is a subacetate of copper. The following table gives the composition of different specimens, as determined by BERELIUS and PHILLIPS (WATT'S "Chem. Dict."):—

	Calculated.	French. Berzelius.			English. Phillips	
					Crystallized.	Compressed.
$2CuO$,	160 ..	43·24 ..	43·34 ..	43·5 ..	43·25 ..	44·25
$C_4H_6O_3$,	102 ..	27·57 ..	27·45 ..	29·3 ..	28·30 ..	29·62
$6H_2O$,	108 ..	29·19 ..	29·21 ..	25·2 ..	28·45 ..	25·51
Impurities,		—	—	2·0	—	6·62
	370	100·0	100·0	100·0	100·0	100·0

The common verdigris of commerce is procured by treating copper plates with acetate of copper, and then covering them with the skins of grapes undergoing acetic fermentation. The plates are removed at intervals learnt by experience, and, after washing, again subjected to the same operation. The verdigris formed on the plates is then scraped off and dried. As a pigment it is bad, though when protected by good varnish from the action of foul gases and moisture it has considerable durability. In oil painting it should never be used mixed with other pigments; it is sometimes admissible as a glaze used with a varnish vehicle. The author, in examining a painting by TINTORETTO, found large quantities of copper in some of the darker parts of the picture; these, when used, were evidently greenish, but had changed in time to brown by the decomposition of the copper pigment.

Stannate of Copper.—This pigment has been suggested as a substitute for arsenic greens, and if carefully prepared rivals them in richness of tint. It may be prepared by first bringing to a red heat in a crucible a mixture of 100 parts of nitre with 59 parts of tin; dissolving the cooled mass in dilute caustic lye, and permitting the solution to clear by standing. This is then further diluted, and added to a solution of sulphate of copper. The dark-brown precipitate at first formed soon changes to a bright green. Another method is also in use, which is said to produce a better result. A solution of 118 parts of tin in nitro-muriatic acid is added to a solution of 250 parts of sulphate of copper, and the mixture is precipitated by caustic soda. This precipitate requires careful washing and drying.

Zincate of Copper (?).—M. HABICH, in the *Technologiste*, describes the preparation of a blue-green compound containing zinc and copper. He does not give the analysis of this body; but from its mode of preparation it would appear to be a zincate of copper. "When neutral nitrate of copper," he says, "is decomposed by an insufficient proportion

of a solution of carbonate of potassium, the flocculent precipitate of carbonate of copper at first formed is gradually transformed into a subnitrate of copper, which precipitates in the shape of a heavy green powder. If this basic salt of copper be treated with a solution of oxide of zinc in potassium hydrate, there is formed a dark-blue colour, which is extremely light and has great covering power. It appears to be a zincate of copper with a very small portion of a highly basic nitrate of copper.

"In order to render this process practical, the operation will be conducted as follows:—

"Copper scales are calcined in a reverberatory furnace, or a muffle, until all the suboxide (Cu_2O) is transformed into monoxide (CuO); that is to say, until a sample dissolves in nitric acid without the production of red nitrous vapours. If the nitric acid contains hydrochloric acid, which is often the case, the silver which may be present in the copper scales will be precipitated in the form of chloride, and may then be collected.

"The solution of nitrate of copper is heated, and decomposed by a clear solution of carbonate of potassium. As soon as the effervescence diminishes in intensity, the solution of carbonate of potassium is added by small quantities at a time, until there remains but little undecomposed copper in the solution. In order to collect the remainder of the metal, the clear liquor is decanted, and the green precipitate is washed several times with small quantities of water. All the liquors are collected, and the remaining copper is precipitated by a solution of potash. The green carbonate of copper is introduced into a new solution of nitrate of copper, in which it is transformed into a basic salt. The previous liquors are evaporated and leave crystals of nitrate of potassium.

"An economical solution of oxide of zinc is made as follows:—Clippings of metallic zinc are treated in a cast-iron vessel with a caustic solution of potash or soda. Hydrogen is immediately disengaged, and the alkali becomes saturated with the oxide of zinc, which plays the *rôle* of an acid. When the liquor is clear, it is employed for the decomposition of the basic nitrate of copper. The product is a handsome and light Bremen blue, and the evaporated liquor, when potash has been used, gives crystals of nitrate of potassium.

"The advantage of this process is based principally upon the preparation of a cheap nitrate of copper (since nitric acid may at a moderate cost be extracted from nitrate of soda), and upon the production of nitrate of potash, which is a valuable secondary product."

Basic Sulphate of Copper.—The author is not aware that this body, which has a lively light green tint, has been used as a pigment; but it excels, both in purity of colour and in permanency, many of the copper greens hitherto described. It can be easily produced by boiling hydrate of cupric oxide, produced by precipitating a cupric salt with caustic soda or potash, with a strong solution of sulphate of copper.

Erlaa Green.—Contains hydrated oxide of copper, chromate of lime, and sulphate of lime.

Elsner Green.—This seems to be stannate of copper, with some vegetable yellow.

German Green without Arsenic.—Many attempts have been made to produce green pigments for wall paper decorations, possessing the brilliancy of arsenical green, but free from that ingredient. We subjoin Struve's analysis of such a green:—

Chromate of lead,	13·65
Basic carbonate of copper,	80·24
Oxide of iron,	0·77
Carbonate of lime,	2·65
Water,	2·58
	99·89

It will at once be seen that such a mixture is quite unfit for artistic purposes, and must be very fugitive.

Mineral Green Lake.—This pigment, improperly called a lake, is prepared by precipitating with carbonate of potash a mixture of chloride of copper and nitrate of zinc. The precipitate is subsequently calcined, and the mass ground to a fine powder.

Borate of Copper.—The precipitate obtained by mixing a solution of borax with one of sulphate of copper, after careful washing and ignition (fusion must be avoided), affords a yellow-green, which becomes darker the longer the ignition is continued. This pigment has little body, and is objectionable on many grounds.

Rinman's Green, Cobalt Green.—This beautiful and permanent pigment is a compound of oxide of zinc and oxide of cobalt. It may be prepared by mixing together the nitrates of zinc and cobalt, and precipitating the mixture with carbonate of potash. The pink precipitate is carefully washed and dried, and then ignited in a crucible at a very high temperature, when its tint changes to green. It is very necessary to use pure chemicals to obtain a good result. The best proportions for a good deep pigment are 9 to 10 parts of oxide of zinc with 1 to 1·5 parts of protoxide of cobalt. It may be also prepared by moistening oxide of zinc with a solution of a cobalt salt, calcining the dried preparation, and washing the mass. R. Wagner, in the *Technologiste*, recommends that the cobalt solution should be precipitated as a phosphate or arseniate. He says—"If the cobaltic solution be precipitated by the phosphate or arseniate of potassium, the phosphate or the arseniate of cobalt thus produced possesses the property of imparting a green coloration to zinc white, at a temperature much lower than that necessary with the ordinary protoxide of cobalt. Moreover, the monoxide of cobalt seems to have gained more body. The green is also of a purer colour and brighter. The alkaline arseniates act like phosphoric and arsenic acids. If before the calcination a small proportion of arsenious acid be added to the ordinary mixture, the calcined mass will be of an exceedingly bright green; and its structure being loosened by the volatilization of the arsenious acid, it will be easy to grind."

The subjoined analyses of specimens of Rinman's green are given by Wagner:—

Oxide of zinc,	88·040
Oxide of iron,	0·298
Monoxide of cobalt,	11·662
	100·000

	I.		II.
Oxide of zinc,	71·93	....	71·68
Monoxide of cobalt,	19·15	....	18·93
Phosphoric acid,	8·22	....	8·29
Soda,	0·69	....	—

Chrome Greens.—The oxides and hydrated oxides of chromium form pigments varying in hue from grey-green to most vivid and pure green. There are many methods of procuring these oxides, a few of which we shall indicate:—

(1) By heating chromate of ammonium. Ammonia is driven off in this operation, oxygen is absorbed from the air, and the oxide of chromium is left behind, retaining the form of the original crystals, which gives it the appearance of green tea. When finely-powdered and ground in oil, it forms a deep but somewhat grey-green paint.

(2) By decomposing bichromate of potash with hydrochloric acid in just sufficient quantity to combine with all the potash.

(3) By heating bichromate of potash until it is decomposed. The potash may be then dissolved out with water, and the oxide of chromium will remain as a fine powder.

(4) To a boiling concentrated solution of bichromate of potash sublimed sulphur is added by small quantities at a time. The gelatinous hydrate formed, after being well washed, is calcined to drive off the water of hydration. Or a mixture of equal parts of powdered bichromate and sulphur is heated in a crucible to redness, and subsequently lixiviated with hot water.

(5) By decomposing chromate of mercury. When neutral proto-nitrate of mercury is treated with bichromate of potash, an orange precipitate is thrown down. After washing and drying, it is finely powdered and introduced into a retort. Mercury in the metallic state is drained off on the application of heat, and may be condensed by passing it into water. The oxide of chromium left behind is a fine green, of great depth of tint.

(6) By calcining a mixture of 3 parts of neutral chromate of potash with 2 parts of sal-ammoniac. Ammonia is driven off, and green oxide of chromium remains mixed with chloride of potassium. The latter may be removed by treating the mass with hot water.

(7) Finely powdered bichromate of potassium is mixed with its own weight of potato starch, and calcined at a high temperature. The chromate is reduced to the state of sesquioxide, and carbonate of potash is formed, which may be removed by washing. A further calcination of the dried oxide produces a pigment which is said to have a fine colour, and to work well as a paint.

(8) A mixture is made with 45 parts of gunpowder, 240 parts of perfectly dry chromate of potash, and 35 parts of sal-ammoniac. This is pressed into moulds and ignited. After elutriation a bright oxide of chromium is left behind.

(9) When powdered bichromate of potash is heated with strong sulphuric acid until oxygen ceases to be given off, a basic sulphate of chromium is left behind. This body is insoluble in water. It has a fine apple-green colour when prepared with care, and might be used safely as a pigment. When this body is boiled with strong soda or potash it undergoes decomposition, sulphate of potassium being formed, and chromic oxide in the state of a fine powder. Thus prepared, the powder, after washing and drying, has a somewhat bluish hue. With oil it forms a deep transparent green paint with great tinctorial power. The author has performed many experiments on this process for making greens, and recommends it strongly to colour-makers, as he feels sure that very favourable results can be obtained.

Veridian, Chrome Emerald Green.—These beautiful pigments are hydrated oxides of chromium. They contain, however, phosphoric or boracic acid, even after long-continued washing with hot water. A specimen of *Vert de Guignet*, examined by Shipton, contained as much as 12 per cent. of boracic acid. M. Guignet directs that it should be prepared by calcining at a red heat a mixture of 3 parts of boracic acid and one part of bichromate of potash. On treating the resulting mass with hot water, uncombined boracic acid is dissolved out along with borate of potassium. Chromate of soda may be used instead of the potassium salt; the product, however, has a lighter tint. M. Arnaudon recommends a mixture composed of 128 parts of neutral phosphate of ammonia and 149 parts of bichromate of potash. This is mixed with a small quantity of water to form a magma, and gently heated until on cooling a brittle mass is formed. This mass, after being broken to small pieces, is heated to a temperature between 180° C. and 200° C. for about half an hour. Ammonia and water are given off, and, provided the temperature is not raised higher than 200° C., a bright green oxide of chromium is formed. Water removes the phosphate of soda, leaving the pigment in the state of a fine powder. Prepared in this manner the product is finer in tint, and more to be recommended than the *Vert de Guignet*.

These greens are all stable, being unaffected by admixture with other pigments, or by contact with foul gases or damp. Veridian produced by M. Arnaudon's process is quite equal in tint to the finest Schweinfurt green, and has none of the faults of that pigment. The author has analyzed several specimens of this green, prepared and sold by Messrs. Winsor & Newton, of Rathbone Place, London, and has found them to be perfectly stable and trustworthy; he is induced to make this remark from the fact that he has heard that some artists fear the durability of this pigment.

Mixed Greens.—These pigments, known frequently as *Brunswick greens*, sometimes called *Chrome greens*, are, as has been already stated, mere mixtures of blue and yellow pigments. Thus, *Hooker's greens*

are mixtures, in varying proportions, of Prussian blue and gamboge. *Milory green*, *silk green*, *leaf green*, &c., also belong to this category. None of these pigments are fit for artistic purposes, as they are wanting in stability. The green paints, known as *Cinnabres*, also belong to this class. These are for the most part made in France, and contain chrome yellow and Prussian blue; they are very unstable, and must not be confounded with the green oxides of chromium already treated of. Mixed greens can be prepared with ultramarine and cadmium yellow; yellow ochre, or Mars yellow or cobalt blue, may be substituted for the ultramarine. Such mixtures are stable, provided the constituents are themselves pure.

Titanium Green.—This pigment, which is a ferrocyanide of titanium, has been recommended as a substitute for Schweinfurt green, but it is far from being as brilliant in tone. It is prepared by adding ferrocyanide of potassium to a very acid solution of titanium chloride. As this precipitate is decomposed at 100° C., care must be taken in drying it.

Vanadium Green.—This pigment is also a ferrocyanide, and is prepared in a similar manner to the last product. It is finer in colour than titanium green. At present, however, on account of the rarity of vanadium, the compound is not used in the arts.

Uranium Green.—The hydrated uranoso-uranic oxide is of a grey-green colour, possessing no brilliancy. Some ores of uranium contain green crystalline masses, which appear to consist of the sulphate of the metal, along with lime and copper. As pigments these compounds are useless.

Molybdenum Green.—When molybdate of sodium is added to a solution of chrome alum, a light green precipitate is thrown down, which is at first somewhat gelatinous, but on washing becomes pulverulent. As a pigment it has no special advantages. There is also a molybdate of copper, which is of a pale-green tint.

Manganese Green.—This is a manganate of barium. It may be prepared by igniting nitrate of barium with peroxide of manganese, or by adding baryta water to a solution of permanganate of barium, and allowing the mixture to stand. As a pigment it is not to be relied upon, as the manganates are unstable bodies.

Green Ultramarine.—This body is produced in the manufacture of artificial ultramarine, which is described later. It is a light-bluish green, but does not seem to have found favour with artists. It is said to be quite stable, provided the vehicles compounded with it are not acid, or do not produce acid by decomposition.

Green Lakes.—These fugitive colours are prepared from the juice of buckthorn berries, the leaves of the woad plant, and many other vegetable greens. There are many varieties; but all are unstable. *Sap or bladder green*, *Iris green*, *Venetian green*, *grass-green*, *China green*, belong to this class. The last named has a reputation for stability; but it is ineligible as a pigment. Many of the pigments sold as green lakes are mixtures of yellow lakes with Prussian blue.

Blue Pigments.—*Native Ultramarine.*—This most beautiful of all blue pigments is obtained from *lapis lazuli*, a mineral of somewhat rare occurrence. The finest samples of the mineral are obtained from Prussia, China, and Great Bucharia. It has usually an earthy bluish-grey tone, enlivened with pure azure and deep blue. It contains not unfrequently small glittering crystals of iron pyrites, which at first gave rise to the idea that the blue colour was in some way due to the presence of iron. It is now, however, well ascertained that such is not the fact. To procure the blue pigment free from the earthy matters with which it is intimately mixed, it is first necessary to reduce the mineral to a fine powder. This is greatly facilitated by heating the substance and cooling it by immersion in water or vinegar. It is then ground in a mill. The powder is mixed with a pasty composition prepared with resin, wax, and linseed oil. This mass is placed in a cloth and kneaded under hot water. The first portions of colouring matter expressed are generally dirty; but as the operation proceeds, the brighter portions make their way through the cloth. Inferior qualities succeed. These are carefully collected and classified. This operation is tedious; but hitherto no better method has been suggested. It would seem that the ultramarine adheres less to the composition than the grey earthy matter with which it is associated. This pigment is very expensive, owing not merely to the rarity of the mineral, but also to the labour required in its preparation. For purity of tone and stability it has no rival.

For a long time the composition of this body remained a mystery to chemists. The analyses did not give any clue to the nature of the colouring matter. Chemists were stimulated by prizes to find a method of preparing the pigment artificially; after long investigation perseverance was rewarded and an *artificial ultramarine* was produced, which if not equal to the native body in purity of tone, is but little removed from it. It would appear that a memoir, published by Gmelin in 1828, gave the key to its ready production. In fact, that chemist gave a formula for manufacturing it which has only been varied in minor details by the best makers of the present day. M. Guimet was the first to introduce a marketable product, and the colour produced by his method still holds high rank in the trade. The process actually followed out by Guimet is still kept secret; but other methods of manufacture are known in detail, some of which we proceed to give. They have been collected from Malepeyre's "Practical Treatise on the Manufacture of Colours for Painting."

There are two operations in the manufacture—1st, the production of green ultramarine; and 2nd, the conversion of this into the blue pigment. The ingredients used are a *good clay* of the kaolin type; one containing little iron is sought for. This is most important. It should approximate as nearly as possible to the composition of a silicate of aluminium.

Gritty particles, and foreign matter generally, is removed by washing and floating. It is then calcined and reduced, by grinding, to a fine powder. Pure crystallized *sulphate of soda* rendered quite neutral is employed. The crystals are slowly dried, to expel water of crystallization. This is also ground and passed through sieves. *Anhydrous carbonate of soda* and dry *sulphide of sodium*. Refined *sulphur*, ground to a powder, and *carbon*. This latter may be wood charcoal or a good bituminous coal, with a small percentage of ash. This is also ground to a fine powder. These bodies are thoroughly mixed together in right proportions. Manufacturers vary on this point, each preferring an admixture which he considers to be the best. Some discard the *carbonate of soda* altogether, some do not use the *sulphate*, and some use a *polysulphide of sodium*, and thus avoid the addition of *sulphur*. The following formulæ are in use:—

	I.	II.	III.
Clay,	100	100	100
Sulphate of soda,	83 to 100	—	41
Carbonate of soda,	—	100	41
Sulphur,	—	60	13
Coal,	17	12	17

Dry *sulphide of sodium* may be substituted in part for the carbonate of soda or the sulphate; 80 parts may replace 100 of carbonate, or 60 parts 100 of the sulphate.

The mixture is then calcined in clay crucibles. This is perhaps the most important part of the manufacture. The regulation of the temperature of calcination, and its duration, are acquired by practice and observation alone. The crucibles are piled on each other in specially-built ovens, resembling small porcelain kilns. If the calcination has been properly conducted, the material shrinks and becomes grey or yellowish-green. The contents of the crucibles are then lixiviated in water, and the insoluble portion washed until it loses every trace of a soluble sulphide. This is ascertained by testing the wash water with a lead salt. If no black precipitate is produced, the absence of sulphide of sodium is ascertained. The porous residue is then ground with water, and again washed. After drying, it is stamped and passed through fine sieves. It is now ready for the second operation — the transformation into blue ultramarine. This is effected by calcining the green product with fresh sulphur. In Germany this is carried out in iron or clay cylinders built into a furnace, and furnished with agitators. The powder is brought to a low heat, and sulphur is thrown into the cylinders. Air is admitted, and the sulphur burns. Specimens are taken from time to time, and the operation is stopped when the ultramarine has attained its greatest intensity of colour. In France this operation is performed in muffles. The product is again washed with water to remove sulphate of soda, which is produced in large quantities in this operation. Such is the general outline of the manufacture of this beautiful pigment. Chemists still differ as to the cause of the colour, but a general opinion is that it is owing to sulphide and hyposulphide of sodium. Different samples vary greatly on analysis. The following by GMELIN is an example:—

Soda and potash,	12·863
Lime,	1·546
Alumina,	22·000
Silica,	47·306
Sulphuric acid,	4·679
Sulphur and loss,	12·218
	100·612

Cobalt Blue, Gahn's Ultramarine.—This fine blue pigment is a compound of alumina with oxide of cobalt. It is of variable composition. It is prepared by mixing solutions of alum and chloride or nitrate of cobalt together, and precipitating the mixture with carbonate of soda. After careful washing and drying the pink precipitate is heated in a crucible to a high temperature, when it assumes a deep-blue colour. In artificial light it has a purple tinge.

Thénard's Blue is another compound of cobalt, containing phosphoric acid and alumina. Basic phosphate of soda, added to a solution of a cobalt salt, produces a violet or pink precipitate. This is mixed intimately with alumina whilst still gelatinous, and the mixture, after drying, is heated to a high temperature in a crucible. There is a modification of this blue in which arsenious acid takes the place of phosphoric acid. Like GAHN'S blue, it has a purple tone when viewed by artificial light.

Cœruleum.—This pigment is of a light sky blue with a somewhat greenish tinge, and is well adapted for painting transparent skies. The process of manufacture is kept secret. It gives on analysis—

Stannic acid,	49·66
Oxide of cobalt,	18·66
Sulphate of lime, &c.,	31·68
	100·00

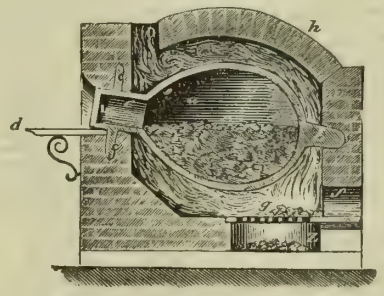
This colour does not appear purple under artificial light.

Smalt Zaffer Blue, Saxony Blue. — This is a glass coloured with silicate of cobalt. There are many qualities of this pigment in the market; but its use in artistic painting is limited. With oil it is said to have a tendency to turn green, and even black. In fresco painting it stands well. It is prepared on the large scale by mixing zaffer, prepared from arsenical ores of cobalt, ground to a fine powder with sand and potash. The mixture is placed in pots, such as are used for the manufacture of glass, having a hole in the bottom which can be closed with a plug. The pots are placed in a furnace, and their contents brought into a state of fusion. Three layers are formed, the middle one being smalt. The upper layer, or dross, is skimmed off with iron ladles, and the lower layer is removed through the opening before mentioned. The glass is then ladled into water, which partially disintegrates it. It is then ground and floated. In purchasing, small colour-makers should be warned that several samples have been sent to the author for analysis, which have been largely adulterated with the cobalt blue containing phosphoric acid. As the pigment is costly, it would, before purchasing, be well to have the sample tested for phosphoric acid.

Copper Blues, Blue Ashes, Mountain Blue, Lime Blue.—All blues having copper for their basis are fugitive, or quickly turn green, and in time black. Blue ashes are prepared by precipitating a solution of sulphate of copper with milk of lime. Mountain blue is a native carbonate of copper known as azurite.

Prussian Blue.—As this well-known pigment is necessarily connected with the manufacture of ferrocyanide of potassium, a short account of the chief processes in vogue for procuring this salt will not be misplaced here. This body, better known as prussiate of potash, is a double cyanide of iron and potassium, having the formula K_2FeCy_6. Animal matters, such as hoofs, dried blood, skin, hair, horn, &c., are used to furnish the requisite nitrogen and carbon. In practice, these organic matters are previously calcined on account of the large quantities of ammonia which they yield; sufficient nitrogen, however, is retained for the production of the cyanogen. The charred substances are made into a paste with a strong solution of carbonate of potash, and the mixture is dried. The potash is thus brought into close contact with the nitrogenous matter. The mixture is then heated in a cast-iron retort, whose sides are very thick. The iron necessary for the formation of the salt is thus procured from the retort itself. Fig. 11 will show the general

Fig. 11.



arrangement of the retort and furnace. *a* is the body of the retort, supported in the back wall of the furnace, *g*, by the projection *b*; the neck, *e*, has two projections, *c c*, which serve to hold the retort in position; *i* is the lid, and *d* is a working plate of stone or iron. The retort is half filled with the mixture, and gently raised to a red heat. The lid is then adjusted, and the fire regulated so as to keep a steady temperature. From time to time the pasty mass is stirred with a rabble. On uncovering the mouth of the retort, combustible gases escape and take fire; as the process nears completion this emission of gas diminishes, and at length ceases. The charge is then ready for withdrawal. This is effected by means of an iron scroop. The pasty mass is placed in an iron box and closed up, so as to prevent contact with the air until quite cool. It is then ready for lixiviation with hot water. When thoroughly disintegrated, the yellow solution is filtered from the residue of charcoal; and if the salt is required to be crystallized, is set to evaporate in suitable pans. As the iron for the ferrocyanide is supplied from the retort itself, it is gradually worn away. It then becomes necessary to turn it half round on its axis, and thus present a new surface. There are many more economical methods of manufacturing this salt, too numerous to mention.

The yellow liquid above mentioned contains some impurities—chiefly carbonate, phosphate, chloride, sulphide, and sulphocyanide of potassium; but for the manufacture of common Prussian blue, the makers do not take the trouble to purify it by crystallization, but the crude solution is immediately added to a solution of sulphate of iron, which has been partially peroxidised by exposure to the air. There results a light blue precipitate, which becomes dark Prussian blue by the absorption of oxygen from the air. The carefully-prepared pigment for artistic purposes should be procured from pure materials.

Antwerp Blue is a carefully prepared Prussian blue.

Indigo.—This colouring matter is of vegetable origin, and is derived from the leaves of a number of plants indigenous to India and Mexico. Amongst these may be mentioned the *Indigotifera argentea*, the *Indigotifera tinctoria* (which is cultivated in France), the *Polygonum tinctorium*, and the *Nerium tinctorium*. The leaves of the plant are steeped in water, and compressed between boards. Fermentation sets in, and the water becomes green. The clear solution is decanted from the sediment, and a sufficient quantity of lime water added until all colouring matter is precipitated. The precipitate is carefully washed. The powder is of a violet-blue colour, and when exposed to the air is permanent. Turpentine is said to partially bleach it. Weak acids do not act upon it, but it is easily dissolved in Nordhausen sulphuric acid. It is easily sublimed in needle-shaped crystals in closed vessels; and as the commercial article is seldom pure, this mode of purification ought to be used in preparing the pigment for artistic purposes. With oil it loses its tone, but is a very useful colour when mixed with gum or size.

Indigo Carmine—Holland or English Blue.—These blues seem to be mixtures of indigo, Prussian blue, smalt, and chalk, thickened with starch or flour.

Browns and Blacks.—*Mars Browns.*—These are produced, as stated under *Red Pigments*, by calcining at a high temperature sesquioxide of iron, prepared either by precipitation or by calcining the sulphate of iron. There are also brown ochres; these sometimes contain manganese. Their preparation for painting is the same as described under *Yellow Ochres.*

Manganese Brown.—Binoxide of manganese or artificially-prepared sesquioxide form very good browns. Some specimens of the mineral known as wad, which is an ore of manganese containing much combined water, give beautiful browns after careful calcination.

Prussian Brown is prepared by carefully calcining Prussian blue in a closed retort.

Ulmin Browns.—These colours are procured by partially carbonizing certain organic matters. There are several ways of preparing them—by acting on alcohol with caustic soda, and heating for a few

hours; by heating sugar and potash together, and subsequently treating with hydrochloric acid. Peat, cotton, and wood-soot yield a brown when treated with alkalies and starch, &c., when treated with strong acids. *Bistre*, a pigment used in water-colour drawing, is the soot produced in burning beech wood. This must be well washed, to remove all soluble matters.

Iron Brown.—The author has obtained a beautiful semi-transparent brown from the deposit found at the bottom of *caustic pots*. It seems to be produced by the decomposition of the ferrate of sodium formed in the manufacture of white caustic. After washing out the adhering soda, the sediment should be passed through a silk sieve to remove particles of dirt and graphite, and then floated.

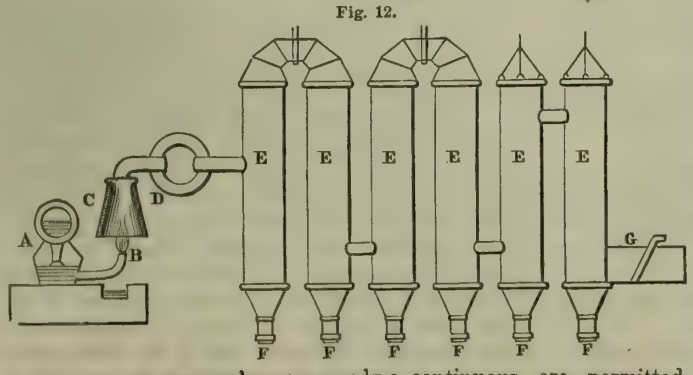
Bitumen, Asphaltum.—Bitumen is found in many parts of the world, but the bitumen of Judea is the kind most usually employed for artistic purposes. It is found on the surface of the Dead Sea. It is soluble in turpentine; but when mixed with oil, dries badly and cracks. It is frequently mixed with wax when prepared as a paint. It should never be used as a pigment; Sir David Wilkie's pictures, where it was largely used, are cracking in many places.

Umber.—This pigment is found native in the island of Cyprus. It is a hydrated compound, containing silica, iron, and manganese. The heavier impurities are removed by floating. When calcined, the water of hydration is expelled, and a darker brown is produced, known as *burnt umber*. *Sienna earth* has already been mentioned under *Yellow Pigments*. When calcined, *burnt Sienna* is produced, which has a brownish-red hue.

Charcoal blacks are produced by the dry distillation of grape stalks, wine lees, peach stones, cork cuttings, &c. These all produce different qualities of brown-blacks, which are ground in water to a fine powder for use.

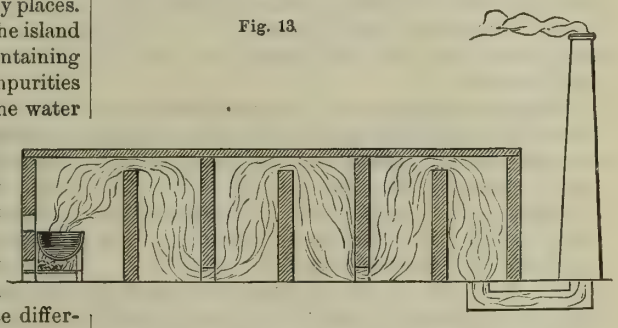
Lamp Black.—This black pigment is obtained by condensing the smoke given off in the imperfect combustion of vegetable oils, resin, coal tar, or the *dead oil* obtained by the distillation of coal tar. The finest qualities are obtained from burning vegetable oils. An apparatus employed for this purpose is shown in the accompanying engraving (Fig. 12).

Fig. 12.



A is a lamp, so arranged as to supply a continuous stream of oil at the level of the wick, B; C is a funnel connected with a vessel, D, in which water and other liquids are condensed; EEE, &c., are sacks, joined by tubes, as shown, in which the soot is deposited; G is a pipe, connected with a chimney stack, to produce a draught of air through the arrangment; FFF, &c., are plugs for removing the product. In the first two sacks the lamp black is usually found to be contaminated with oils and salts; but in the others, if the operation has been well conducted, the product is found to be a fine soft black, nearly free from foreign admixture. It is a matter of importance to regulate the draught, as the contents of the sacks run the risk of being inflamed if the admission of air is too rapid, whereas an insufficient supply would not allow the smoke to pass through the apparatus. The dead oils from coal tar may be burnt in like manner, and produce a good quality of lamp black. Where large quantities are produced, the apparatus described above is not used; but the oils are burnt in a pan, and the products of combustion are carried through a series of chambers, communicating alternately at the top and bottom by the draught created by a chimney (Fig. 13). The lamp black is deposited on the walls

Fig. 13.



and floors of these chambers, and is periodically removed. Thus prepared, this pigment is contaminated with greasy substances of a complex nature, which, if not removed, greatly impair its drying qualities. The usual plan adopted is to calcine the product in iron cylinders, which, for convenience, are formed in two portions hinged together. Further treatment with dilute hydrochloric acid and subsequent washing with water remove any soluble salts. From experiments which are now in hand, the author believes that this method of purification, which is cumbersome and expensive, may be altogether dispensed with by using a liquid which will dissolve the fatty matters adhering to the carbon.

Blacks from vegetable sources are very numerous.

Bone Black, Ivory Black.—These are prepared by carefully calcining bones or ivory in close retorts. After all gaseous matter is expelled, the contents of the retorts are permitted to cool, and then subjected to careful grindings.

PLATINUM — *Platine*, French; *Platin*, German. Atomic weight, 197·6. Symbol, Pt. This metal is not very abundant. The first account of it with which we are acquainted is that of ANTONIO D'ULLOA, in 1736, who observed it in the auriferous sands of South America. Among the metallurgists of South America, however, it was long known, and bore the name *platina*—a diminutive of the Spanish name (*plata*) for silver.

The principal districts which afford platinum are Brazil, Peru, Antioquia, and the slopes of the Ural Mountains. In Borneo, and in almost all the gold-washing districts throughout the world, traces of the metal have likewise been detected. Along the coast of the South Sea, and on the western slopes of the Cordilleras of the Andes, between the second and sixth degrees of north latitude, platinum occurs; but the most productive washings are those of Condoto, in the province of Novita, of Santa Rita or Viroviro, of Santa Lucia, of the ravine of Iro, and Apoto, between Novita and Taddo. In the provinces of Matto Grosso and Minaes Geraes in Brazil, platinum is found in the alluvial deposits which produce gold. The veins of manganese in the weathered syenite near Santa Rosa de Osos, in the Columbian province of Antioquia, afford platinum; and it has been obtained from the valley of the river Jacky in Saint Domingo.

Platinum washings in the Ural Mountains were established in 1824, and since that period considerable quantities have been annually produced by them; they are situated on the western slopes of the chain of mountains, and the ore is met in alluvial deposits partly, and in other localities injected into the greenstone and serpentine rocks.

Platinum, though invariably found in the metallic state, has never been discovered pure and unalloyed. It is generally met with in small grains; but considerable masses of the metal have occasionally been discovered.

The ores of platinum contain the following substances: — 1. Sand. The whole of the sand is never removed by washing the ore; and is found to have associated with it zirconium, ferric chromate, and in the Russian ores ferric titanate.

2. Iridium osmide.

3. Platinum, iridium, rhodium, and palladium, combined no doubt in the form of an alloy. To these SERGIUS KERN has lately added a new metal, which he calls Davyum.

4. Copper and iron, which exist in the ores in a metallic state, for the iron found in the sand is not soluble in acids

5. Gold, and oftener than is supposed a little silver. The latter metal is generally found with the palladium; it is very rare that the palladium is obtained quite free from silver when it is prepared by the old processes.

The following methods of analysis are pursued by DEVILLE and DEBRAY:—

To estimate the sand a small assay crucible is glazed on the inside with a little borax: 7 to 10 grams. of pure granulated silver and 2 grams. of the ore are introduced, and over the platinum 10 grams. of fused borax and one or two small pieces of wood charcoal are placed. The silver is now melted, and care must be taken to keep it for some time a little hotter than the melting point, so that the borax may be very liquid, and may dissolve the vitreous matters which accompany the platinum and constitute the sand. The crucible is now allowed to cool, and when it is cold, the button, which will contain all the silver, osmium, platinum, and all the other metals, is detached, and, if necessary, digested for a time with weak fluoric acid to remove any traces of borax. It is now heated to redness and then weighed. The weight of the button subtracted from the sum of the weights of the ore and silver employed, will give the amount of sand in the ore.

To estimate the iridium osmide, heat 2 grams. of the ore with aqua regia at 70° C. until the platinum is entirely dissolved. The aqua regia must be renewed occasionally for twelve or fifteen hours, or until it is no longer coloured. The solution must be decanted with the greatest care from the metallic spangles of iridium osmide, and the sand which remains at the bottom of the beaker. If necessary it may be filtered; but as little as possible of the osmide must be allowed to fall on the paper. The insoluble residue must be washed by decantation, then dried and weighed after having added what remained in the filter. By subtracting from the weight of this residue the weight of the sand obtained in the former operation, the amount of the iridium osmide is obtained. The button obtained in determining the sand may be employed, in which case the silver is to be dissolved out with nitric acid, and the residue treated as directed above.

To determine the platinum and iridium, the solution in aqua regia from the last operation is evaporated to dryness at a low temperature, and the residue is redissolved in a small quantity of water, to which is added about twice as much alcohol (if it should not entirely dissolve in the water some more aqua regia must be added, and the evaporation repeated); lastly is added a great excess of sal-ammoniac in crystals. The whole is then slightly warmed to promote the solution of the sal-ammoniac, well stirred, and afterwards set aside for twenty-four hours.

The orange-yellow, or even reddish-brown, precipitate which is formed, contains the larger part of the platinum and iridium; some, however, remains in the solution. The precipitate must be thrown on a filter and washed with alcohol. Afterwards the filter with its contents is dried and heated to low redness in a platinum crucible, and finally burnt at the lowest possible temperature. Once or twice after the incineration of the filter a piece of paper saturated with turpentine should be introduced into the crucible, by which means the oxide of iridium will be reduced, and the expulsion of the last traces of osmium be effected. The crucible is now heated to whiteness until it no longer loses weight; or the reduction is finished in a current of hydrogen.

The liquid, separated from the platinum yellow by filtration, is evaporated until the ammonium chloride crystallizes in great quantity. It is allowed to cool, is then decanted, and on a filter is collected a small quantity of a deep violet-coloured salt, which is the ammonium chloride of iridium mixed with a little platinum salt. The mixture of platinum and iridium obtained by the two reductions is then weighed. The two metals are next digested at about 40° or 50° C. in aqua regia, which is renewed until no longer coloured. The residue is pure iridium.

This method of separating the two metals is very accurate if the aqua regia is very weak, and the contact with it is prolonged.

The palladium, iron, and copper are next sought for. The liquor, charged with sal-ammoniac and alcohol, from which the platinum and iridium have been separated, is evaporated to get rid of the alcohol, and then treated with an excess of nitric acid, which transforms the ammonium chloride into nitrogen or hydrochloric acid. It is now evaporated almost to dryness. The residue is removed to a weighed covered porcelain crucible. When the matter is dry it is moistened with concentrated ammonium sulphide, and afterwards dusted over with two or three grams. of sulphur. When dry, this crucible is placed within a larger one of clay, and surrounded with pieces of wood charcoal. The two crucibles are now set in a cold furnace, which is filled up with charcoal, and the fire is lighted at the top to avoid the projection of any of the contents of the crucible, which might occur if it were too quickly heated. After reaching a bright red heat the crucibles are allowed to cool. The porcelain crucible now contains palladium in a metallic state, with the sulphides of iron and copper, forming at the same time a little sulphuric acid. The solution of the nitrates is poured off from the residue, which is then washed by decantation, and the solutions and washings are evaporated to dryness, and then calcined at a red heat. In this way the palladium is reduced, and the iron and copper pass to the state of oxides, which are easily separated from the palladium by means of strong hydrochloric acid. The palladium remains in the crucible; it is again strongly ignited, and then weighed.

The chlorides of iron and copper are evaporated to dryness at 100° C., and are then treated with ammonia. The ferric chloride, having lost nearly all its acid, has become insoluble, but the chloride of copper is readily dissolved, and may be filtered from the iron, which is washed, ignited, and weighed.

The copper solution is next evaporated to dryness, mixed with excess of nitric acid, and heated to drive off excess of ammonium chloride. Afterwards the nitrate of copper is ignited and weighed. The weight of the copper is so small that the hygrometric water absorbed may be neglected.

The residue insoluble in nitric acid is weighed and treated with very dilute aqua regia, which takes up the gold, and sometimes, but very rarely, traces of platinum. To ascertain if platinum be present, evaporate to dryness, and redissolve by alcohol and chloride of ammonium. If any platinum yellow remain, it must be ignited and weighed. The difference in the weight of the porcelain crucible before and after the treatment with aqua regia gives the weight of the gold, from which, if any be found, the weight of the platinum must be deducted.

The residue left in the crucible is rhodium, which must be reduced in a current of hydrogen.

The operator should avoid breathing the vapour from the aqua regia, and as much as possible guard against the ill effects of the osmic acid, which particularly attacks the eyes.

ANALYSES OF PLATINUM ORES.

	(DEVILLE AND DEBRAY).						(S. KERN.)	
	Columbia.	California.	Oregon.	Spain.	Australia.	Russia.	Russia.	
Platinum,	80·00	79·85	51·45	45·70	59·80	77·50	80·03	
Iridium,	1·55	4·20	0·40	0·95	2·20	1·45	9·15	
Rhodium,	2·50	0·65	0·65	2·65	1·50	2·80	0·61	
Palladium,	1·00	1·95	0·15	0·85	1·50	0·85	1·20	
Gold,	1·50	0·55	0·85	3·15	2·40	—	—	
Copper,	0·65	0·75	2·15	1·05	1·10	2·15	1·02	
Iron,	7·20	4·45	4·30	6·80	4·30	9 60	6·45	
Iridium osmide,	1·40	4·95	37·30	2·85	25·00	2·35	(0·28)	Ruthenium.
Sand,	4·35	2·60	3·00	35·95	1·20	1·00	—	
Osmium,	—	0·05	—	0·05	0·80	2·30	1.35	
Total,	100·15	100·00	100·25	100·00	99·80	100·00	100·09	

PREPARATION OF PLATINUM.—When obtained directly from the ore the difficulty of preparing the metal pure increases according to the number of other components associated with it; if the platinum be alloyed only with gold, all that is necessary is to treat it at once with nitro-hydrochloric acid till the whole is dissolved, to remove the excess of acid by evaporation, and then produce ammonium platino-chloride by the addition of ammonium chloride. If other metals be united with the platinum, as in the samples of which the analyses have been given above, then the ore is alternately treated with strong nitric and hydrochloric acids, till all the copper, iron, lead, and silver, manganese, &c., are removed; the washed residue is then acted upon with aqua regia till the whole of the metals dissolve. A moderately dilute solution of sal-ammoniac is now added to the clear filtered liquid, which should, however, be as free of acid as possible, and the precipitate collected, washed well with cold water, dried,

and reduced to the metallic state. The latter operation is effected by gently heating the mass at first, and indeed till the whole of the ammoniacal salt is expelled, and subsequently bringing it to a strong red heat. The residue will now be pure metallic platinum in a very finely-divided condition, or, as it is ordinarily termed, *platinum mohr—platinum black*. The rhodium, palladium, osmium, and iridium, provided a little nitric acid be added previous to precipitation, remain in the mother-liquid, and can be recovered subsequently.

Pure platinum has a white colour, nearly approaching to that of silver. Its density is the greatest of any known body; its specific gravity being 21·5. It is infusible at the highest temperature of a blast furnace, though capable of being welded like iron at a white heat; the temperature of the flame of the oxyhydrogen blowpipe, however, as also that of the voltaic arc, readily melts and even boils it, dispersing a portion into vapour, which appears to burn and form an oxide of the metal. DUMAS observed that platinum becomes harsh and brittle when heated powerfully in contact with charcoal, owing to its combination with a little carbon, or silicon, or phosphorus. Platinum is very malleable, and therefore can be beaten out into very thin plates, and drawn into wires $\frac{1}{20\,000}$th of an inch in diameter; and with proper means, such as inclosing it within a silver wire, into wire only $\frac{1}{30,000}$th of an inch. Air and moisture have no effect upon the metal even in the heat; unlike gold and silver, sulphur and mercury do not injure it even when intensely heated. Potassium nitrate, and potassium and lithium hydrates, at a high temperature, oxidise it; but it remains uninjured by the strongest simple acids. The combination of hydrochloric with any other of the mineral acids dissolves it readily; so likewise does chlorine water, or a mixture of a chloride or nitrate, and of nitric or hydrochloric acid, and in every instance a dichloride, $PtCl_2$, of the metal results. With phosphorus, arsenic, antimony, bismuth, cadmium, tin, and lead, platinum forms alloys at moderately high temperatures; and if the heat be increased it combines even with silver and copper.

Spongy platinum is of a dull grey colour, soft, and porous; when ignited strongly it adheres together, and by subjecting it to pressure with hard bodies, it is made into the form of laminæ, having the metallic lustre. Without any apparent change in itself, it induces the combination of gases, or the oxidation of bodies, to a remarkable extent. DÖBEREINER was the first to discover this remarkable fact. DULONG and THÉNARD showed that this metal, in the more compact form of fine wire and foil, is capable of inducing the union of oxygen and hydrogen in a limited degree, and FARADAY has shown what precautions are necessary to be observed to insure success in the trial—namely, cleanliness of the metal effected by fusing potassium hydrate on its surface, and after washing in water, rinsing it in hot oil of vitriol, and again with water. In this state platinum foil will act upon a mixture of the two gases in the proportion of one volume of oxygen and two of hydrogen, so as to speedily become red hot. Contact with the skin, a cloth, or mere exposure for a few days, divests it in a great degree of this property; so likewise do sulphuretted hydrogen, carbonic oxide, and olefiant gases.

Platinum has, besides the power of causing the ignition of oxygen and hydrogen gases, that of condensing gases upon its surface to a surprising extent. Thus, when exposed to the air, platinum absorbs oxygen gas to the extent of many times its volume; on nitrogen it has but little effect.

There are several forms of finely-divided platinum which exhibit greater power of condensation of gases than spongy platinum. Such is the product resulting from the combustion of bibulous paper which had been saturated with a solution of platinous chloride, and dried, and that produced by voltaic action in an acid solution of dichloride of platinum by a bar of zinc; but the most remarkable for this effect is the platinum black of LIEBIG. This is prepared by boiling dichloride of platinum solution with an excess of potassium hydrate or sodium carbonate of soda. On pouring alcohol gradually into the solution a black precipitate falls in a finely-divided, and probably in a more amorphous state, than any of the other compounds. When this body is well washed and dried, it takes up as much as 250 times its volume of oxygen, and if absolute alcohol be dropped upon it in this state ignition immediately takes place. The combustible gases are quickly inflamed by it, and spirits of wine energetically acetified. When treated with dry ammoniacal gas it is rendered red hot, and a considerable quantity of ammonia is absorbed.

METALLURGY OF PLATINUM.—At St. Petersburg, where the platinum of all the ore found in the Ural is extracted, the following process is pursued:—Into each of a number of open platinum basins capable of holding 8 lbs. each, that are ranged on a sand-bath covered by a glazed dome with movable panes, surmounted by a ventilator which carries off the liberated acid vapours, a certain quantity of the material is introduced, and a mixture composed of 3 parts of hydrochloric acid 42° Twaddell, and 1 of nitric at 73° Twaddell, poured upon it. The whole is then heated during eight to ten hours, or till the evolution of red fumes ceases; and after allowing the undissolved matter to subside, the liquid is decanted into a large cylindrical vessel, the residue is washed with water, and the washings added to the first liquor. The undissolved matter is treated with further quantities of acid till the whole becomes soluble, and the liquors commingled in the common receptacle already mentioned. Aqua regia to the amount of from ten to fifteen times the weight of ore operated upon is required, according as the granules of the ore are smaller or larger in bulk. Moderately dilute ammonia liquor is now added to the acid liquor in the glass vessel, when a precipitate occurs, and on its subsidence the supernatant liquor is decanted into other vessels and evaporated to about one-twelfth in glass retorts, embedded in a sand-bath; on allowing this liquor to

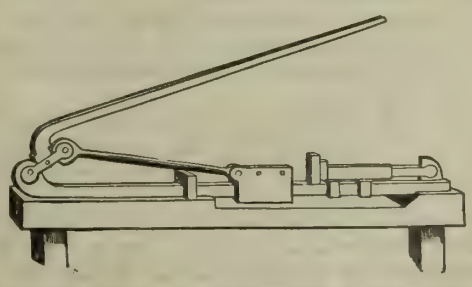
cool the double chloride of ammonium and iridium crystallizes out in the form of a dark purple powder, which is separated, and the mother-liquor evaporated to dryness in porcelain vessels, the residue calcined and treated anew like fresh ore. The precipitate obtained in the first instance is dried, calcined, and heated to redness for obtaining the metal in a spongy state. In order to agglomerate this sponge, it is pounded in a bronze mortar, the powder passed through a fine sieve, and the product introduced into the mould in which the ingot is to be formed. Here it is compressed with a rammer which is forced in by a coining press, and when reduced to the proper size, it is removed from the mould and baked for thirty-six hours in a porcelain kiln, after which it may be forged with ease, provided the iridium had been separated from it. The ingot of platinum contracts to the extent of one-sixth or one-fifth of its volume during the roasting in the oven.

WOLLASTON'S method, of which the preceding is a modification, is best calculated to yield the pure metal. The ore is treated with aqua regia and ammonium chloride, as in the preceding case; only, to prevent the solution of the iridium it is necessary to dilute the acids, so that it may remain in the residue. It is well to reduce the strength of the hydrochloric acid with an equal quantity of water, and the aqua-fortis and muriatic acid must be quite pure. WOLLASTON has indicated that a quantity of hydrochloric acid, equivalent to 150 of dry acid, and as much nitric acid as will contain 40 parts, is sufficient for the solution of 100 parts of the platiniferous matter; but as it is best to have an excess of the ore, 120 parts of the latter should be employed. The action of the compound acid should take place slowly, and a very gradually increasing temperature be applied till the operation be completed, which happens in about four days. After this the contents of the vessel are allowed to repose, in order that the iridium scales may deposit; this done, the clear solution is to be drawn off, and after the separation of any subsided matter, 41 parts of ammonium chloride are added, when the yellow crystalline ammonium platino-chloride falls. This precipitate weighs 165 parts, and contains 66 parts of platinum. Palladium, iridium, rhodium, ruthenium, osmium, gold, silver, iron, and any other foreign matters, are all or in part contained in the mother liquor from the last precipitate, together with 11 parts of platinum. To obtain the latter the whole of the metals are precipitated by means of a clean plate of zinc or of iron, the metallic deposit well washed, redissolved in aqua regia as before, and the platinum thrown down with ammonium chloride, after having added 1 part of strong hydrochloric acid to every 32 parts of the liquor, with the view of preventing the palladium and lead from falling down with the yellow platinum salt. By a later method, WOLLASTON neutralizes the acid solution with carbonate of soda, and precipitates the palladium from the liquid with cyanide of mercury, in the form of whitish flakes. When this is removed by filtration, the platinum may be removed from the mother liquor by the addition of 41 parts of ammonium chloride.

The precipitate from the first liquor, as well as that from the re-solution of the residuary matter in aqua regia, is well washed with cold water, quite free from the ammonium iridio-chloride; it is then dried carefully by pressure between folds of bibulous paper or other absorbent matter. After the whole of the moisture is dispersed, the substance is introduced into a black-lead crucible, and subjected to a temperature merely sufficient to expel the ammonium salt and chlorine. Should the heat be raised too high, it would cause the agglutination of the metal, so as to render its subsequent compression into ingots difficult, at the same time that it would decrease its welding power. The loose platinum powder is next rubbed between the palms of the hand very gently, sifted through a linen cloth, and the coarse particles that remain behind reduced in a wooden dish with a pestle of the same material, with as little force as possible. This portion is then sifted like the rest, and the fine powder, which ought not to exhibit any metallic lustre, or the finer parts, may be separated by elutriation and decantation. Having sufficiently reduced the mass, it is mixed with water to a pastelike consistency, and introduced into a brass mould or cylinder 6·75 inches high, 1·12 inch wide at the top, and 1·23 at the bottom, which is inclosed by a steel stopper that enters it to the distance of a quarter of an inch, having the inner face smeared with grease. The whole is now wrapped round with bibulous paper, and placed in a vessel of water so as to fill it with the liquid, when the metal sinks and fills every portion of it equally, and cavities in the ingot are avoided.

A piece of bibulous paper is now laid on the top of the platinum, and then woollen cloths, and the excess of moisture removed by pressing the contents of the cylinder by a wooden pestle forced by the hand. The cloths and paper are removed at this stage, and a disc of copper substituted, the paste having sufficient consistency to allow the mould to be placed horizontally in a press, to be condensed preparatory to its forging. The kind of apparatus which WOLLASTON invented is represented in Fig. 1. After the pressure is sufficiently exerted, the cylinder

Fig. 1.



is opened, and the ingot, shaped in the form of the cylinder, taken out without danger of breaking in

the hands, and heated nearly to redness in a charcoal fire, in order to drive off moisture, burn the grease, and give it greater compactness. It is then laid endwise on a clay support, strewn over with quartz sand, and introduced into a blast furnace. Twenty minutes' ignition is given, and whilst still red hot the ingot is taken from the furnace, placed upon an anvil endwise, and struck with a hammer repeatedly. Should it bend under this treatment, it must not be straightened by striking it in a horizontal position; but the blows must be directed on the edges so as to rectify the bend, and still preserve it straight. After the ingot is sufficiently condensed by this means, it is in a position to bear forging and working into any desired shape, like any other metal.

DEVILLE and DEBRAY treat the ores both in the dry and wet way. In the former case they employ a reverberatory furnace having a hemispherical fire-clay bed. This is heated to full redness, and the charge, which is 2 cwts. of the platinum ore, intimately mixed with a like weight of plumbic sulphide (galena) is thrown in by slow degrees, being at the same time constantly stirred about with an iron rake. A small quantity of glass is afterwards added to serve as a flux, and finally 2 cwts. of litharge is added in small quantities. The oxygen thus supplied combines with the sulphur of the galena, forming sulphurous acid, which passes off. The reduced lead combines with the platinum metals, forming a fusible alloy. After a little time the osmiridium sinks to the bottom, and the platiniferous lead is then skimmed off in iron ladles and cast in ingot moulds. The lead is removed by cupellation, and the platinum finally refined by fusion on a bed of lime.

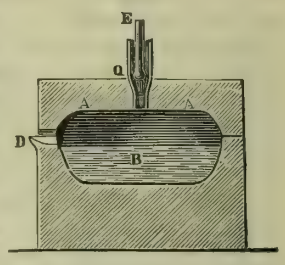
In the wet way the platinum ore is treated with aqua regia, separated from the insoluble osmide of iridium by decantation, and the solution evaporated to dryness. The red residue is then heated to redness in a covered crucible, with a tubular cover to convey the vapours to a chimney shaft. The platinum powder remaining is washed and refined on a lime bed in the manner described below.

Platinum of commerce also frequently retains traces of silicon and osmium. DEVILLE and DEBRAY remove these by fusion on lime, by means of an oxidising flame. The silicon is converted into calcium silicate, which melts into a colourless bead, and moves rapidly about on the surface of the metal until it reaches the edge, when it is absorbed by the sides of the furnace.

Platinum, thus melted and refined, is a metal as soft as copper; its density, 21·15, is less than that of ordinary platinum, which has been subjected to hammering.

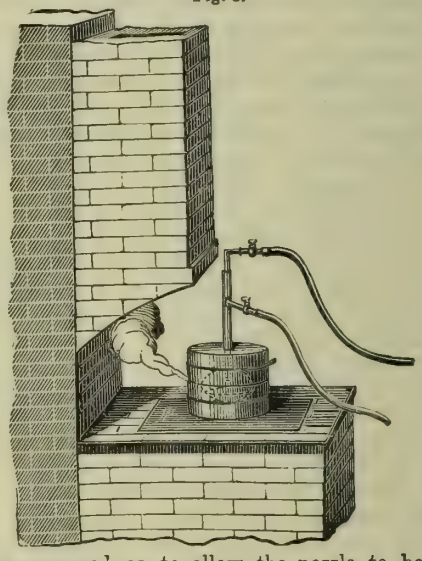
The fuel employed in DEVILLE and DEBRAY'S furnace is most commonly coal gas; but hydrogen may be employed, and when pure will give a greater heat. The combustion is fed by a current of oxygen. The furnace in which the fusion is made is of lime, bound with iron wire. Figs. 2 and 3 show the arrangement of the parts of a small furnace; Fig. 4 shows a larger furnace. The small furnace, Figs. 2 and 3, is composed of two parts—the roof, A A, made of a cylindrical piece of lime, slightly arched on its lower surface, and pierced by a conical hole, Q, through which a blow-pipe, E, is made to pass; and a bottom, B, made of another piece of lime, hollowed out as shown in the cut. The cavity should be scooped out so deep that the melted platinum may occupy a depth of 3 or 4 mm. At the anterior part, D, a groove, inclined a little towards the inside, is made with a file; this serves as an outlet for the metal when fused, and for the flame whilst the process is going on.

Fig. 2.



The blow-pipe (shown in detail in Fig. 4) is composed of a copper cylinder, E E, terminated at its lower extremity by a slightly conical tube, E′ E′, made of platinum. A copper tube, C C C, having a platinum nozzle, enters the first cylinder at P; and

Fig. 3.



is so arranged as to allow the nozzle to be slid up or down, and placed at any height within the cylinder, E E, E′ E′, that may be wished. A stop-cock, H, is attached to the side of the cylinder, E, by means of a tube as large as the cylinder itself. Another stop-cock, O, terminates the elbow of the tube, C. The hydrogen, or coal gas, passes into the furnace by the stop-cock, H, and the oxygen by the stop-cock, O.

When the fusion is to be made, the pieces of lime composing the furnace are put together; then holding the blow-pipe in the hand, the stop-cock, H, is opened, so as to allow the passage of a gentle stream of gas which is lighted, and the stop-cock, O, turned to admit the oxygen. The flame is in this way plunged into the apparatus by the hole, Q, in such a manner as to avoid an explosion, which might

disturb the position of the pieces of lime. The body of the furnace is now gradually heated, the quantity of the gases passing being increased by degrees until the maximum temperature is attained. The degree of heat may be raised or lowered at pleasure, by lifting or depressing the platinum nozzle which supplies the oxygen.

The temperature is now lowered, and the platinum is introduced, little by little, through the opening, D. When in thin slips, the metal melts directly it enters the furnace. The oxygen should be at a sufficient pressure to give a rotatory motion to the molten metal, so as to equalize the temperature throughout the mass.

When it is not wished to run the metal into a mould, the two gases are turned off by degrees, always leaving the oxygen in a decided but very slight excess, so soon as the fusion is perfect and the refining completed, which is the case when no more vitreous matter is seen to form on the surface.

The mass now gradually solidifies, and the flame may be completely extinguished. A little of the metal is always thrown up on to the roof of the furnace; this is easily collected.

When the platinum is to be cast, an ingot mould is prepared of thick cast iron well rubbed with plumbago, or of lime or coke. The last are most easily made of sawn plates of the substance, held together by iron wire. The roof of the furnace is taken off, the body seized with a pair of tongs, and the platinum poured off without hurrying. The only difficulty which occurs (and this a little practice enables the operator to overcome) is to discern at the same time the dazzling surface of the metal and the open mouth of the mould, before turning up the crucible. A larger quantity than 3 or 4 kilogrammes should never be cast in this way, as there would be great danger of some part of the apparatus giving way.

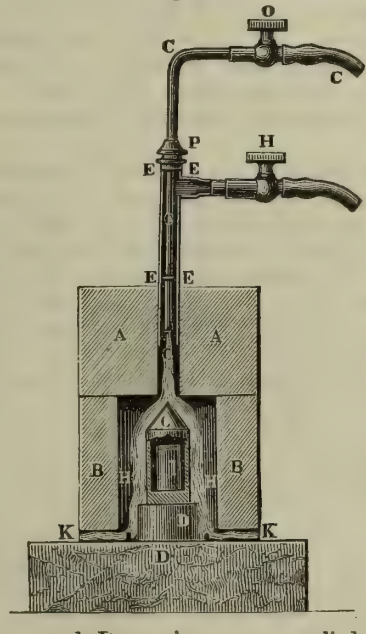
For greater quantities a larger furnace is necessary. This is constructed of three pieces of good sound lime, bound firmly together with iron (Fig. 4). The lower one, D, forming the base, is a circular plate of about 2½ inches thickness; this carries a cylinder, B, about 4½ inches in height, and having four apertures, K, at the lower part for the escape of the gases, vapours, &c., evolved during combustion. This piece is the furnace chamber. Upon its upper end is placed a third piece, A A, which covers the chamber, and is about 3 inches thick, and perforated by a round hole in the centre for the passage of the compound jet of the blow-pipe, E E, which has been already described. Inside the chamber is placed an outer crucible, formed also of lime, and provided with a conical lime cover, G. This stands upon a small lime support, D′, and incloses the actual crucible, I, which is formed of gas coke, and has a cover of the same material. The flame of the blow-pipe laps round the two crucibles in the centre of the chamber, H H, and escapes at K.

JOHNSON and MATTHEY have fused as much as 2½ cwts. of platinum in this furnace at one operation.

When large castings are made in iron moulds, it is necessary to protect the latter from fusing under the enormous temperature of the liquid platinum. HERAENS obviates all inconveniences arising from this cause by placing at the bottom of the mould a thin leaf of platinum, which supports the first contact of the metal.

Lime is used for several reasons as the material for constructing the refining furnace. It conducts heat so sparingly that through a thickness of 0·8 inch, the apparatus being full of melted platinum, the temperature of the outside is barely 120° C. It radiates heat most perfectly. For this reason it is the best material for the sides of a reverberatory furnace of this kind. It acts on all the impurities of the platinum, iron, copper, silicium, &c., changing them into fusible compounds, which are absorbed by its porous substance.

Fig. 4.



DEVILLE and DEBRAY'S process, applied to the revivification of old platinum, gives excellent results. No foreign metal, except iridium and rhodium, can exist in platinum after it has been melted and refined in the method described. All the substances which most easily attack platinum—such as sulphur, phosphorus, arsenic, gold, sodium, iron, copper, palladium, osmium—are separated either by oxidation and absorption by the lime, or by volatilization. Gold and palladium escape in the form of vapour, and may be collected by making the flame which issued from the furnace pass through an earthenware tube.

The only caution necessary to be observed in the process is never to have the bath of metal at all deep, without keeping it in constant agitation; since, as the platinum is a bad conductor of heat, it will not remain liquid to any great depth, and there will be a chance of the refining being incomplete.

The metals associated with platinum have particular characters, which separate them more or less completely from the other metals. They are never found apart from each other except, and this but rarely, in the case of palladium. More or less alterable under the influence of oxygen and chlorine, they are all allied by the facility with which they are reduced. Besides, they have the curious property of determining many chemical reactions by their simple contact—their *catalytic* action. This last property cannot be ascribed to the porosity of the metal, for platinum which has been melted is as active as platinum black.

OSMIUM.—Atomic weight, 199·2. Symbol, Os. Osmiridium, placed in a porcelain tube, is heated to bright redness in a current of air. The two metals are oxidised, the ruthenium oxide remains in the tube, whilst the osmium tetroxide (osmic acid, OsO_4) is carried forward and condensed in a solution of potash. This solution is mixed with excess of hydrochloric acid and digested with mercury in a well-closed bottle at 40° C. An amalgam is formed, which when distilled in a stream of hydrogen leaves the osmium in the form of a black pyrophoric powder (Berzelius). Its specific gravity is about 7.

Deville and Debray powder the osmiridium, if in scales, by calcining them with 4 or 5 times their weight of zinc. This powder is mixed with $5\frac{1}{2}$ times its weight of barium dioxide, and the mixture heated to the temperature of molten silver for two or three hours. The black mass thus formed is placed in a glass retort, a little water added, and afterwards 8 parts of hydrochloric and 1 part of nitric acids. These are well shaken together and distilled, taking care to keep the receiver well cooled to avoid the escape of osmic acid. When the vapour has no longer the smell of osmic acid, the distillation is stopped, and the liquid in the receiver is distilled afresh, and the product is condensed in dilute ammonia.

The ammonium osmiate is supersaturated with sulphuretted hydrogen, and the liquor containing the osmium sulphide is boiled for some time and then filtered.

The osmium sulphide, dried at a low heat, is placed in a crucible of coke, which is itself inclosed in another crucible of refractory clay, and then heated for four or five hours to the temperature of melted nickel. The sulphide is reduced, and there is left a brilliant metal of a blue colour. If the heat is raised to that of melted rhodium, the metal has the density of 21·3 to 21·4. This osmium is without smell, and only becomes combustible at a temperature higher than that of melted zinc.

When osmium is dissolved in zinc, and the zinc afterwards separated by hydrochloric acid, osmium is obtained in a very combustible amorphous powder; but when the zinc is volatilized, and the residue fused in the oxyhydrogen gas furnace, the osmium is found completely metallic; it is not melted, but is full of irregular cavities. This osmium scratches glass easily. At the temperature of melting iridium osmium volatilizes; but no traces of fusion can ever be discovered.

RUTHENIUM.—Atomic weight, 104·4. Symbol, R. After osmium, it is the most refractory metal known. It requires a very extreme heat to melt the smallest quantity; when melting, the dioxide. RuO_2 is formed, which is volatilized, and smells something like osmic acid. When removed from the flame ruthenium is blackish-brown on the surface, and is brittle and hard like iridium. Its density is 11 to 11·4 after long fusion.

To prepare the metal the osmide is mixed in fine powder, with 3 parts of barium dioxide and 1 part of barium nitrate, and heated to redness in a clay crucible for an hour. The black friable mass is powdered and introduced into a flask containing 20 parts of water, mixed with 10 of hydrochloric acid. The flask must be placed in cold water during the reaction. When this is finished 1 part of nitric acid and 2 parts of strong sulphuric acid are successively added. The flask is well shaken, and the barium sulphate allowed to settle. The precipitate is washed by decantation, and the liquid and washings are distilled together in a tubulated retort, until about one-fourth of their volume of a liquid very rich in osmic acid has passed over. The red liquor left in the retort is evaporated to a small volume, 2 or 3 parts of ammonium chloride in small pieces are added, and a little nitric acid. The whole is then evaporated to dryness at the temperature of boiling water. A crystalline violet-black precipitate remains, which is treated with a little water containing ammonium chloride, and washed with the same solution until no longer coloured.

The insoluble salt left is heated by degrees to redness, and the mixture of iridium and ruthenium thus obtained is fused in a silver crucible with an equal weight of potassium hydrate and twice its weight of potassium nitrate; and when cold, the potassium rutheniate is dissolved out with cold water. The solution, which is yellow, is decomposed by means of carbonic or nitric acid, and the precipitated oxide of ruthenium is strongly calcined in a charcoal crucible. The ruthenium is then reduced in the oxyhydrogen gas furnace.

PALLADIUM.—Atomic weight, 106·5; symbol, Pd.—This is the most fusible of all the platinum metals. The gas furnaces easily bring it into a liquid state; and when heated to the temperature of fused iridium, it disappears, giving off green vapours, which condense into a bistre-coloured dust, being a mixture of the metal and its oxide. Heated in contact with the air, and kept in a state of fusion in an oxidising atmosphere, it spits like silver at the moment of solidification. It is more oxidisable than silver, and tarnishes in the air. The density of pure palladium, melted but not hammered, is 11·4.

RHODIUM.—Atomic weight, 104·4; symbol, Rh. —Rhodium is obtained by fusing platinum residues with an equal weight of lead and twice its weight of litharge. When the crucible has attained a bright red heat, it is shaken once or twice, and allowed to cool slowly. The button of lead is treated

with nitric acid, diluted with an equal volume of water, which removes, besides the lead, the copper and palladium also. The insoluble powder remaining is mixed with five times its weight of barium dioxide, and heated to redness in a clay crucible for two or three hours. It is then treated with aqua regia to remove the osmium. When the liquor has lost all smell, sufficient sulphuric acid is added to exactly precipitate the baryta. It is then boiled, filtered, and evaporated to dryness, first adding to it a little nitric acid, and then a great excess of ammonium chloride. The residuum is washed with a concentrated solution of ammonium chloride, which removes all the rhodium.

When the washings are no longer coloured, the liquor is evaporated with a great excess of nitric acid, which destroys the sal-ammoniac; and when only the rhodium salt is left, the evaporation is finished in a porcelain crucible.

The rhodium salt is now moistened with ammonium sulphide, mixed with three or four times its weight of sulphur, and the crucible heated to bright redness, after which metallic rhodium remains.

Thus obtained, the rhodium is nearly pure, after it has been boiled for some time first in aqua regia and then in concentrated sulphuric acid.

To obtain it perfectly pure, it must be melted with four times its weight of zinc. The alloy is then treated, first with hydrochloric acid, and the residue with aqua regia, and to the last solution ammonia added till the precipitate first formed is redissolved. The solution is boiled and evaporated, by which is obtained the yellow salt, or rhodium chloride. This is purified by repeated crystallization, and then calcined with a little sulphur, by which means rhodium is procured absolutely pure.

Rhodium melts less easily than platinum; it is not volatilized, but oxidises on the surface like palladium. Its colour and appearance resemble aluminium. When perfectly pure, it is ductile and malleable. Its density is 12·1.

IRIDIUM.—Atomic weight, 198; symbol, Ir.—The ammonio-chloride of iridium, containing ruthenium, obtained in the preparation of the latter metal, is dried and calcined in a current of hydrogen. Platinum and part of the osmium are extracted by aqua regia, and the ruthenium is separated by fusion with nitric and potassium hydrate, followed by prolonged washing in water. The osmium which remains is removed by placing the metal in the oxidising flame of the blow-pipe, and the metal is then melted in the lime furnace, using, however, pure hydrogen in place of coal gas.

The colour of iridium is pure white, somewhat like steel. It breaks under the hammer at the temperature of the air, but becomes malleable when raised to a white heat. Its density is 21·15.

POTASSIUM. — *Potassium*, French; *Kalium*, German and Latin. Atomic weight, 39·1; symbol, K.

Isolated by Sir HUMPHREY DAVY, in 1807. He obtained it by the action, on the slightly moistened hydrate (caustic potash), of a powerful voltaic current produced by about 200 pairs of WOLLASTON'S plates—the metal appearing at the negative pole, while oxygen was evolved from the positive electrode. The compound nature of the hydrate had long been suspected; but while it was confidently anticipated that it would ultimately be decomposed and demonstrated to be an oxide, it was not until the experimental proof was given that the existence in it of a new and peculiar metal was realized. The discovery of this metal was one of the most important of the age, and the application, by DAVY, of similar methods of investigation to the hydrates of sodium, barium, strontium, and calcium, resulted in the separation of these metals, which till then were unknown.

Distribution and Sources.—On account of its intense affinity for the non-metallic elements, potassium is never met with in nature in the free state; but its compounds are both plentiful and widely distributed. The two great, and indeed the only original sources of these, are the sea and the primitive rocks, all others being intermediate. Sea water contains 1 part of the metal in 1500, combined as chloride and sulphate; and in these forms it is absorbed and concentrated by marine plants, in the ash of which, and particularly in that of the *Laminaria* and *Fuci*, the salts exist in great proportion, and are extracted on a large scale. In the same states of combination it occurs in the "abraum," or potash salts, immense beds of which overlie the great rock-salt deposits of Stassfürt and Douglashall in Prussia. These are the result of the protracted evaporation of inland seas, and now constitute by far the most important source of the potash products of commerce. Rock salt contains it in appreciable quantity, and its salts are sometimes found, associated with that substance, in a concentrated form; as at Kalusz, near Stanislau, in East Galicia, where enormous quantities have been manufactured for industrial purposes, and in India, in the district of the northern Punjaub. It is also present to a small extent in the "caliche," or crude nitrate of soda, met with in such immense beds in the Iquique district of Peru, and which is probably a product of the oxidation of nitrogenous organic matter in presence of sea-salt; and it is an important ingredient in many saline waters, such as those of Vichy, Seidschütz, and Harrogate. It exists in considerable quantity in some well-defined minerals, such as potash-felspar, alumite or alum-stone, potash-mica, lucullite, and apophyllite, and is contained in small proportion in most clays. Combined with silica, it occurs in the primitive rocks, and by the disintegration of these it finds its way into soils, from which it is absorbed by growing plants, forming an essential part of their mineral food, and is left in various conditions of combination when these are burned. It is found as nitrate (saltpetre) in large quantity, as an efflorescence on and near the surface of soils in India. In wood ashes it is sufficiently abundant to render the extraction of its salts a source of profit. In the juice of the grape it exists in large proportion as bitartrate (cream of tartar), which is deposited, during the fermentation, in the preparation of wine; and in the juice of the

beet-root it is so plentiful, that it is extracted in the form of carbonate, sulphate, and chloride, for manufacturing purposes, from the molasses obtained in the fabrication of the sugar. The mineral portion of flesh is very rich in potassium compounds, which are derived from the vegetable food upon which the animals subsist; and it is present as sudorate in the sweat of sheep, its recovery from the wool, as carbonate, forming a branch of chemical industry.

Preparation.—1. By the action of a powerful voltaic current on the hydrate (Davy). This method is not now resorted to as a means of procuring the metal. 2. By heating to whiteness a mixture of the hydrate with iron borings, and condensing the metallic vapours in rock-oil (Gay-Lussac and Thénard). This process was at one time employed for the preparation of the metal, but is now obsolete. 3. By passing a voltaic current, produced from six Bunsen cells, through a fused mixture of 15 parts of chloride of potassium and 11 parts of chloride of calcium, using carbon electrodes, cooling the crucible, and opening it under the surface of rock oil (Matthiessen). The metal is thus obtained in a state of great purity. 4. By heating to whiteness an intimate mixture of charcoal and potassium carbonate (obtained by calcining crude tartar or "argol" without access of air), when the following reaction takes place:—

$$K_2CO_3 + C_2 = K_2 + 3CO.$$

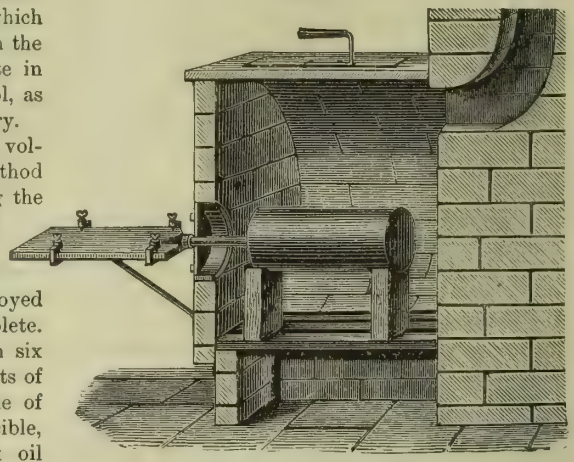
This method was originally devised by Curaudau, but improved by Brünner, and by Donny and Mareska, and is the one at present employed in the preparation of the metal in quantity. It is conducted in the following manner:—Several pounds of the perfectly dry mixture, in the state of lumps, are introduced into a small iron cylinder or bottle fitted with a short iron tube, to which is attached a flat condenser constructed of two iron plates bolted together. The iron vessel with its contents is then placed horizontally in a furnace having a strong draught, and heated gradually to whiteness. Vapours of potassium are soon evolved, and must be condensed as rapidly as possible, to avoid the formation of a large quantity of a violently explosive compound (carboxide of potassium), formed by the combination of the metal with carbonic oxide. This substance has the formula $K_2C_2O_2$, and may be viewed as a compound of rhodizonate and monoxide of potassium, thus:—

Potassium Carboxide.		Potassium Monoxide.		Potassium Rhodizonate.
$5K_2C_2O_2$	=	$2K_2O$	+	$K_6C_{10}O_8$.

The accompanying sketch (Fig. 1) shows the arrangement of furnace, retort, and condenser.

As soon as vapours of potassium cease to be evolved, the receiver is opened under the surface of Persian naphtha to avoid oxidation, the metal removed, and purified by redistillation. About one half of the entire amount of potassium is lost in the operation, to obviate which it has been recommended to use argol containing a considerable quantity of tartrate of lime, or to add to the mixture of charcoal and potassium carbonate about 10 per cent. of chalk. The mixture obtained by calcining

Fig. 1.



the crude tartar should have approximately the following composition:—

Carbonate of potassium,	76
Carbon,	14
Carbonate of calcium,	10
	100

which nearly agrees with the theory.

Properties.—Potassium is a metal having a brilliant silver-white lustre, with a tinge of violet which is just perceptible, but which may be intensified by viewing it with the light reflected several times from its own surface. A freshly-cut surface of the metal appears as brilliant as that of silver, but is almost instantaneously tarnished by the formation of a film of oxide, which for some time protects the subjacent metal from oxidation; and if the operation of cutting be performed in the dark, a faint blue light is seen to be emitted. Its specific gravity is ·865, and it therefore floats on water, which it instantly decomposes, on account of its great affinity for oxygen, with the following reaction:—

$$K_2 + 2H_2O = 2KHO + H_2.$$

The evolved hydrogen is kindled by the heat developed by the action, and continues to burn with a violet flame as long as any metal remains, while the hydrate is retained in solution. At the ordinary temperature of the air it is soft and weldable, and may be easily cut with a knife or moulded into any form; but at 0° C. it is crystalline and brittle. When heated to 62°·5 C. it melts and appears like mercury; and at a red heat it volatilizes, appearing as a green vapour. With sodium it forms an alloy which is fluid at ordinary temperatures, and which may be prepared by treating the hydrate (caustic potash) with the metal sodium in boiling caoutchin. It also yields a crystalline amalgam with mercury. It dissolves in anhydrous liquefied ammonia, producing a blue fluid, which on evaporation in the absence of oxygen leaves the metal unchanged (Seely). On

account of the liability of potassium to tarnish by contact with oxygen in any form, it is generally recommended to keep it in rock oil or Persian naphtha; but its lustre cannot long be preserved in this way. When heated in turpentine which has been repeatedly rectified by distillation with sodium, however, it melts, and on cooling solidifies, forming a mass of obtuse dimetric octahedral crystals, and in this fluid it may be preserved untarnished (CLARK and IRVING). Also, it may be preserved indefinitely, with unimpaired lustre, by hermetically sealing a tube in which a Torricellian vacuum has been produced, taking care that one end is drawn to a fine point, which is then broken under the surface of the melted metal, while the latter is kept covered with a layer of pure paraffin; the tube, as soon as filled, is withdrawn, and the fine point sealed by the Bunsen flame. As usually met with, it is not necessarily free from sodium; a sample analyzed by TATLOCK gave—

	Per Cent.
Potassium,	98·46
Sodium,	1·54
	100·00

Potassium is a monatomic metal, and for all practical and analytical purposes its atomic weight may be taken as being 39·1.

On account of its high price as compared with sodium, and of the great similarity between the properties of the two metals, it has not as yet found any practical application, on the large scale, worthy of the name.

Potassium forms at least four well defined oxides:—Monoxide, K_2O; dioxide, K_2O_2; trioxide, K_2O_3; and tetroxide, K_2O_4: but the researches of LUPTON show that there are others of intermediate composition. These are all solid bodies, and their respective colours are white, brownish-yellow, lemon-yellow, and sulphur-yellow, while the intermediate oxides are grey-blue. The first of these (anhydrous potash) is the only one of sufficient importance to require special notice. It may be prepared, 1. By heating 1 part of the metal in small fragments with $1\frac{1}{2}$ part of caustic potash, when hydrogen is evolved and the oxide remains. 2. By exposing thin slices of the metal, at ordinary temperatures, to the action of dry air free from carbonic acid. 3. By heating mixtures of the metal with certain metallic oxides, or with sulphuric, silicic, boracic, or carbonic anhydride.

HYDRATE OF POTASSIUM (KHO). Synonyms—Hydrate of Potash, Potassium Hydroxide, Caustic Potash; *Hydrate de Potasse*, French; *Kalihydrat* or *Aetzkali*, German.

Preparation.—1. By the action of pure potassium upon water in the absence of nitrogen. Small fragments of the metal are thrown, one at a time, into pure water; hydrogen is evolved, while the hydrate remains in the fluid, which may then be evaporated to dryness, the residue heated to fusion in a silver capsule, in the absence of carbonic acid, and poured out on a silver or polished iron plate. It is thus obtained perfectly pure, but as the method is an expensive one it is not followed, unless the product is required as a special laboratory reagent. 2. By the action of the monoxide on water, thus:—

$$K_2O + H_2O = 2KHO.$$

3. By heating 1 part of pure nitrate of potassium (which is easily obtained by repeated crystallization) with $2\frac{1}{2}$ parts of copper clippings, to moderate redness, for half an hour. The following action takes place:—

$$2KNO_3 + 3Cu_2 = 6CuO + N_2 + K_2O.$$

The residue is then lixiviated with water, the solution evaporated, and the result fused (WÖHLER). According to POLLACCI the product always contains copper, and it is therefore advisable to employ iron in place of that metal. 4. By the mutual action of sulphate of potassium and hydrate of barium, thus:—

$$K_2SO_4 + BaH_2O_2 = BaSO_4 + 2KHO.$$

When the insoluble sulphate of barium has settled, the clear fluid contains only hydrate of potassium. 5. By boiling a moderately strong solution of pure carbonate of potassium with calcined marble, when the following change occurs:—

$$K_2CO_3 + CaO + H_2O = CaCO_3 + 2KHO.$$

The solution contains only the hydrate with a little lime.

The following table (I.) shows the percentage composition, according to TATLOCK, of a sample of "liquor potassæ" and of two samples of "stick potash," all purchased in the ordinary way:—

TABLE I.

	"Liquor Potassæ."		"Stick Potash."	
	Liquor.	Solids from Liquor.	1	2
Hydrate of potassium,	5·37	89·66	70·26	62·00
Carbonate of potassium,	·25	4·17	4·83	11·74
Sulphate of potassium,	trace	trace	·05	·06
Chloride of potassium,	·10	1·66	·67	2·09
Nitrite of potassium,	absent	absent	absent	absent
Hydrate of sodium,	·25	4·17	12·34	15·07
Soluble silica and alumina,	·02	·34	·31	·46
Insoluble matter,	—	—	trace	trace
Water,	94·01	—	11·30	8·83
	100·00	100·00	99·76	100·25
Specific gravity,	1·052			

For ordinary chemical and pharmaceutical purposes, however, it may be obtained by dissolving 1 part of the finest commercial carbonate of potassium in 10 of water, boiling the solution, and gradually adding 1 part of well burned lime previously slaked and made into a cream with water. The solution thus prepared retains any neutral potassium salts, soda, silica, and alumina that may have been originally present in the carbonate employed. The "liquor potassæ" of the British Pharmacopœia is prepared in a similar way. This should have a specific gravity of 1·058, and should contain 5·84 per cent. of hydrate of potassium (KHO). The "stick potash" and "lump potash" of commerce are obtained in this way; the liquor being evaporated to an oily con-

sistence, then heated to fusion, in order to expel water as far as possible, and run into iron moulds.

A comparatively pure hydrate may be obtained by digesting either of the two last-named products with alcohol or methylated spirit, evaporating the solution, and fusing in a silver or polished iron basin (BERTHOLLET). Purified in this way, however, it still contains some chloride of potassium and all the soda originally present.

Manufacture.—"Caustic potash" is now made on a very large scale by a process identical with that followed in the manufacture of "caustic soda" (LE BLANC'S process). Starting with chloride of potassium, a sulphate is prepared by heating it with sulphuric acid, hydrochloric acid being evolved and condensed in the usual way, and the sulphate remaining as a residue. The latter is then furnaced with coal and limestone, and the resulting "black ash" lixiviated, the liquors boiled down, and any sulphate, chloride, and carbonate of potassium, as well as carbonate of sodium, fished out. A little nitrate of potassium is then added—to oxidise salts of the lower sulphur acids, as well as to destroy the organic matter, which gives a brown colour to the fluid—and the concentration continued until the product is comparatively free from water, and solidifies on being cooled. Any kind of sulphate of potassium having a sufficient degree of purity may be employed.

The following table (II.) shows the composition of some samples of caustic potash, analyzed by TATLOCK, representing the article made on the large scale:—

TABLE II.

	White.	Brown or Cream.	
	1.	2.	3.
Hydrate of potassium,	77·64	75·64	74·05
Carbonate of potassium,	4·62	2·54	3·14
Sulphate of potassium,	·38	·21	·69
Chloride of potassium,	2·29	·93	2·26
Nitrite of potassium,	·87	—	—
Hydrate of sodium,	4·67	2·59	3·20
Soluble silica and alumina,	·30	·20	55
Insoluble matter,	·02	·22	·69
Water,	8·84	17·80	15·80
	99·68	100·13	100·38
Potassium in hydrate,	54·11	52·72	51·60
Equal to potash (K_2O),	65·19	63·51	62·17
Potassium in carbonate,	2·61	1·44	1·78
Equal to potash,	3·14	1·73	2·14
Potassium in sulphate,	·17	·09	·31
Equal to potash,	·20	·11	·37
Potassium in chloride,	1·20	·49	1·18
Equal to potash,	1·44	·59	1·42
Potassium in nitrite,	·40	—	—
Equal to potash,	·48	—	—
Total potassium,	58·49	54·74	54·87
Equal to potash,	70·45	65·94	66·10
Total available potassium,	56·72	54·16	53·38
Equal to potash,	68·33	65·24	64·31
Or carbonate of potassium,	100·24	95·71	94·34
Total alkali calculated as potash,	73·83	68·28	68·08
Ratio of sodium to available potassium—potassium, 100,	4·73	2·74	3·35
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100,	5·29	3·07	3·85

Hitherto soft soap manufacturers have, for the most part, prepared their own caustic potash either from the American pot-ashes and pearl-ashes, or from the French and German carbonates, which can be had very strong and pure. Now, however, by reason of the comparatively low price of all potassium salts, there is less inducement to do this, and consequently solid caustic potash will probably soon find a large market. In England caustic potash of high strength is made in large quantity, for manufacturing purposes, by the Greenbank Alkali Co., St. Helens; it is also prepared in France and Germany by a modification of the above process.

Applications.—In addition to its use for the manufacture of soft soap, caustic potash is employed to some extent for the preparation of saltpetre, by treatment with nitrate of sodium, whereby caustic soda is also obtained; and it is used in conjunction with caustic soda in the manufacture of oxalic acid from sawdust. Medicinally it is prescribed, in the form of exceedingly weak solution, as an antacid.

Properties.—Pure hydrate of potassium is a compact, white, solid body, having a specific gravity of about 2·1. When heated to a temperature somewhat under redness it melts to a transparent oily-looking fluid, in which state it is instantaneously destructive to all animal and vegetable substances; and at a white heat it is gradually dissipated in the form of white pungent fumes. The constitutional water which it contains cannot be expelled by exposure to the highest known temperature, and its affinity for water is so intense that great heat is developed when it is dissolved in that fluid. According to BERTHELOT there are 12·46 heat units developed by the solution of one equivalent of the dry hydrate in 100 parts of water. On exposure to the air it quickly absorbs sufficient water to dissolve it, and combines with carbonic anhydride, being converted first into carbonate, and ultimately into bicarbonate. In the solid state it is a powerful caustic; and even its concentrated solution rapidly disorganizes animal and vegetable tissues, on account of its disposition to induce the combination of the elements of water, and from its property of dissolving albumen and similar substances. In the form of a weak solution it has an acrid, pungent taste, and faint but disagreeable odour. It is a powerful alkali, strongly changing reddened litmus to blue, and producing a purple colour with a faint trace of artificial alizarin diffused in water, and with feebly acidified alcoholic solution of cochineal and logwood. From solutions of metallic salts whose hydrates are insoluble it precipitates the latter, replacing them and producing a potassium salt which remains dissolved, and this it does by reason of its strong basic character. With water it forms two well defined crystalline hydrates—$KHO + H_2O$ and $KHO + 2H_2O$. It is soluble in half its weight of cold water. It also dissolves abundantly in alcohol, and freely in wood spirit, fusel oil, and glycerin; but ether takes it up only sparingly. The following tables (III., IV., V., and VI.) give the proportions of hydrate and protoxide of potassium in aqueous solutions of various densities, at 15° C.:—

TABLE III.—CONSTRUCTED BY DALTON AND CONFIRMED BY MEHRENS.

Specific Gravity.	KHO Per Cent.	K_2O Per Cent.
2·4	—	100·0
2·2	100·05	84·0
2·0	86·22	72·4
1·88	75·74	63·6
1·78	67·65	56·8
1·68	60·98	51·2
1·60	55·62	46·7
1·52	51 09	42·9
1·47	47·16	39 6
1·44	43·83	36·8
1·42	40·97	34·4
1·39	38·59	32·4
1·36	35·01	29·4
1·33	31·32	26·3
1·28	27 87	23·4
1·23	23·22	19·5
1·19	19·29	16·2
1·15	15·48	13·0
1·11	11·31	9·5
1·06	5·59	4·7

TABLE IV.—CONSTRUCTED BY TUNNERMANN.

Specific Gravity.	KHO Per Cent.	K_2O Per Cent.
1·3300	33·693	28·290
1·3131	32·345	27·158
1·2966	30·998	26·027
1·2805	29·650	24·895
1·2648	28·303	23·764
1·2493	26·954	22·632
1·2342	25·606	21·500
1·2268	24·933	20·935
1·2122	23·585	19·803
1·1979	22·237	18·671
1·1839	20·890	17·540
1·1702	19·542	16·408
1·1568	18·195	15·277
1·1437	16·846	14·145
1·1308	15·498	13·013
1·1182	14·151	11·882
1·1059	12·803	10·750
1·0938	11·456	9·619
1·0819	10·108	8·487
1·0703	8·760	7·355
1·0589	7·412	6·224
1·0478	5·957	5·002
1·0369	4·717	3·961
1·0260	3·369	2·829
1·0153	2·021	1·697
1·0050	·6738	0·5658

In the above two tables the proportions of hydrate are not originally given, but have been calculated in order to enhance their value.

TABLE V.—CALCULATED BY SCHIFF FROM TUNNERMANN AND DALTON'S RESULTS.

Specific Gravity.	KHO Per Cent.	K_2O Per Cent.
1·036	5	4·198
1·077	10	8·396
1·124	15	12·595
1·175	20	16·791
1·230	25	20·989
1·288	30	25·187
1·349	35	29·385
1·411	40	33·582
1·475	45	37·780
1·539	50	41·978
1·604	55	46·176
1·667	60	50·374
1·729	65	54·572
1·790	70	58·770

In the original table only the hydrate corresponding to the specific gravity is given in each case; but the equivalent of monoxide has been calculated and inserted for comparison with the other tables.

TABLE VI.—CONSTRUCTED BY RICHTER.

Specific Gravity.	KHO Per Cent.	K_2O Per Cent.
1·58	63·19	53·06
1·56	61·43	51·58
1·54	59·65	50·09
1·52	57·71	48·46
1·50	55·32	46·45
1·48	52·88	44·40
1·46	50·39	42·31
1·44	47·84	40·17
1·42	45·22	37·97
1·40	42·86	35·99
1·38	41·37	34·74
1·36	39·85	33·46
1·34	38·28	32·14
1·32	36·61	30·74
1·30	34·94	29·34
1·28	33·18	27·86
1·26	31·37	26·34
1·24	29·50	24·77
1·22	27·56	23·14
1·20	25·31	21·25
1·18	23·03	19·34
1·16	20·72	17·40
1·14	18·31	15·38
1·12	15·84	13·30
1·10	13·43	11·28
1·08	10·95	9·20
1·06	8·36	7·02
1·04	5·68	4·77
1·02	2·90	2·44
1·00	—	—

In this case, as in that of Tables III. and IV., the proportions of hydrate have been calculated in each case, and added to the original.

When solution of caustic potash is quite free from carbonate, it gives no effervescence on being acidified with dilute hydrochloric acid; but in order to determine the respective proportions of the hydrates of potassium and sodium, a complete analysis is necessary.

CARBONATE OF POTASSIUM (K_2CO_3). Synonyms—Potash, Carbonate of Potash, Pearl-ash, Salt of Tartar; *Carbonate de Potasse*, French; *Kohlensaures Kali*, German.

Preparation.—1. By saturating with carbonic anhydride a solution of pure caustic potash, evaporating and igniting the residue. 2. By calcining pure bitartrate of potassium (cream of tartar), lixiviating the residue with water, evaporating the solution to dryness, and exposing the dry substance to a red heat. 3. By heating 1 part of nitrate of potassium (saltpetre) with 2 parts of oxalic acid and a little water, evaporating to dryness, and heating the residue to redness (SMITH).

MANUFACTURE. — For commercial and manufacturing purposes, this salt is obtained from a variety of sources. These are principally wood and plant ashes; "vinasse," or the residue remaining after the fermentation of beet-root molasses; "suint," or the sweat of sheep obtained from the wool; and sulphate of potassium, produced by the decomposition of the chloride by sulphuric acid, or prepared by the action of sulphate of magnesium on chloride of potassium.

1. *From Wood Ashes.* — Potassium in various

states of combination exists in comparative abundance in many land plants; and when the latter are burned its salts remain, forming a portion of the ash. The following table (VII.) shows the proportion of potash in some of the principal woods and vegetable substances, according to VAUQUELIN, PERTIUS, KIRWAN, and DE SAUSSURE.

TABLE VII.

	Per Cent.
Pine,	·045
Poplar,	·075
Beech,	·145
Beech bark,	·600
Oak,	·153
Oak bark of branches,	·420
Box,	·226
Willow,	·285
Elm,	·390
Vine,	·550
Thistles,	·500
Cotton grass,	·500
Rush,	·508
Fern,	·626
Wheat-straw,	·390
Wheat before flowering,	4·700
Barley-straw,	·580
Maize-stalk,	1·750
Bean-stalk,	2·000
Stinging nettles,	2·503
Vetch,	2·750

The following Table (VIII.) shows, according to Höss, the proportions of ash and potash in some of the leading woods and plants:—

TABLE VIII.

	Ash, Per Cent.	Potash, Per Cent.
Pine wood,	·34	·045
Beech wood,	·58	·127
Ash wood,	1·22	·074
Oak wood,	1·35	·150
Elm wood,	2·55	·390
Willow wood,	2·80	·285
Vines,	3·40	·550
Ferns,	3·64	·425

The following Table (IX.), calculated from BERTHIER'S original analysis, shows the composition of pine-tree ash:—

TABLE IX.

		Per Cent.
Soluble in water.	Carbonate of potassium,	1·86
	Sulphate of potassium,	3.63
	Chloride of potassium,	1·88
	Carbonate of sodium,	6·03
	Silica,	·18
Insoluble in water.	Lime,	38·51
	Magnesia,	9·56
	Oxide of iron,	·09
	Oxide of manganese,	·36
	Carbonic acid,	32·77
	Phosphoric acid,	·91
	Silicic acid,	4·19
		99·97

In Canada and the United States of America "pot-ashes" and "pearl-ashes" have been extracted for a very long period from the ash of wood obtained by the burning of the primitive forest timber; and a large proportion of these was shipped from the ports of Montreal, Quebec, and New York to Great Britain, and was chiefly consumed in the manufacture of soft soap, and for general cleansing and scouring purposes. This branch of industry is now much reduced, not only on account of less wood being felled in America than formerly, but by reason of competition with the "carbonate of potash," now made so extensively from the ash of French and German beet-root molasses, and also with the carbonate and "caustic potash" prepared artificially from the sulphate by LE BLANC'S method.

The process of manufacture from wood ash is one not involving much chemical skill; and the proportion of product, as compared with the amount of wood employed, is exceedingly small. On an average, the timber of the pine-tree does not contain more than about 1·25 per cent. of ash, of which less than one-tenth consists of potash; so that to procure 1000 kilos. of the best pot-ashes of commerce, containing 65 per cent. of potash in all forms of combination, 520,000 kilos. of the wood must be consumed, during which process the organic salts of potassium and sodium originally present are converted into carbonate and hydrate, which, with the sulphate and chloride, remain when the combustion is completed. The ashes thus obtained, after being sifted from unburned charcoal, are placed in wood vats or casks provided with a false bottom, and are there lixiviated with the smallest possible quantity of water containing a little slaked lime, in which the carbonate and hydrate are exceedingly soluble, and are thus separated from the greater part of the neutral salts, which are left behind. The liquors are then drawn off by a plug, evaporated to dryness in iron pots, and finally fused by being heated nearly to redness. The greyish-pink compact masses are the "pot-ashes"; they are packed in barrels and assorted, by officially appointed inspectors, into "firsts," "seconds," "thirds," and "unbrandables," according to quality, before they leave the port. In this country they are known as "Montreal," "New York," or "Quebec," according to the port from which they are shipped. "Pearl-ashes" are made by carefully calcining the crude pot-ashes in reverberatory furnaces, during which carbonaceous matter is burned away, the hydrate is carbonated, and any salts of the lower sulphur acids are oxidised to sulphates. The residue is then lixiviated with the minimum quantity of water, the solution evaporated down, and the product stirred during solidification, in order to produce the ash in the form of white granular masses.

In Russia a large quantity of the commercial carbonate is made in a similar manner, both from wood ash and from the ash of straw, the latter being of somewhat inferior quality. In France the lees of wine, and vine stalks, are largely employed for the same purpose; and in Tuscany, Austro-Hungary, and the district of the Vosges, it is made also from the ashes of wood and other vegetable substances: the nature of these, as well as of the methods of incineration, mode of manufacture, and quality and composition of the product, varying in each country or district, which also gives its name to the variety produced in or exported from it. In the following table (X.) will be found analyses, by various chemists, of the leading varieties of pot-ashes and pearl-ashes made from wood:—

TABLE X.

	Montreal Pot-ashes.						
	Firsts.				Seconds.		Thirds.
	1.	2.	3.	4.	5.	6.	7.
Carbonate of potassium,	43·87	26·16	33·79	27·32	38·53	21·71	46·31
Hydrate of potassium,	36·50	50·03	43·02	47·28	30·63	42·44	6·14
Sulphate of potassium,	10·40	15·32	16·07	12·71	18·92	9·18	20·53
Chloride of potassium,	2·43	3·38	1·68	4·41	6·13	12·82	7·63
Carbonate of sodium,	—	—	—	—	—	—	—
Hydrate of sodium,	2·02	2·44	1·67	3·67	5·01	6·75	10·48
Soluble silica, alumina, &c.,	—	—	—	—	—	—	—
Insoluble matter,	1·00	·92	1·38	·80	·54	4·85	8·77
Water,	3·75	1·85	2·20	4·00	trace.	1·80	—
	99·97	100·10	99·81	100·19	99·76	99·55	99·86
Potassium in carbonate,	24·82	14·80	19·12	15·45	21·79	12·28	26·20
Equal to potash (K_2O),	29·90	17·83	23·03	18·62	26·25	14·80	31·56
Potassium in hydrate,	25·44	34·87	29·97	32·95	21·35	29·58	4·28
Equal to potash,	30·65	42·01	36·11	39·69	25·72	35·63	5·15
Potassium in sulphate,	4·67	6·87	7·21	5·70	8·49	4·13	9·21
Equal to potash,	5·62	8·28	8·69	6·87	10·22	4·97	11·09
Potassium in chloride,	1·27	1·77	·89	2·31	3·21	6·71	3·99
Equal to potash,	1·53	2·13	1·07	2·78	3·87	8·09	4·79
Total potassium,	56·20	58·13	57·19	56·41	54·84	52·70	43·68
Equal to potash,	67·70	70·25	68·90	67·96	66·06	63·49	52·59
Total available potassium,	50·26	49·67	49·09	48·40	43·14	41·86	30·48
Equal to potash,	60·55	59·84	59·14	58·31	51·96	50·43	36·71
Or carbonate of potassium,	88·83	87·79	86·76	85·54	76·24	73·98	53·86
Total alkali calculated as potash,	62·92	62·72	62·63	61·10	57·88	58·37	49·05
Ratio of sodium to available potassium —potassium, 100,	2·31	2·82	1·95	4·36	6·69	9·27	19·70
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100,	2·58	3·16	2·18	4·87	7·46	10·38	22·12
Analyst,	TATLOCK.						—

TABLE X. (*Continued*).

	Canadian Pearl-ashes.		Italian Potash.		Russian Potash.		French Potash.
	First Quality.	—	—	Tuscany.	—	—	Vosges.
	8.	9.	10.	11.	12.	13.	14.
Carbonate of potassium,	77·50	71·38	82·38	74·10	69·61	50·84	38·63
Hydrate of potassium,	—	—	—	—	—	—	—
Sulphate of potassium,	11·65	14·38	9·86	13·47	14·11	17·44	38·84
Chloride of potassium,	2·65	3·64	1·05	·95	2·09	5·80	9·16
Carbonate of sodium,	2·86	2·31	4·34	3·01	3·09	12·14	4·17
Hydrate of sodium,	—	—	—	—	—	—	—
Soluble silica, alumina, &c.,	·23	3·29	—	·54	1·07	—	1·20
Insoluble matter,	·26	·44	·65	·65	1·21	3·60	2·66
Water,	4·88	4·56	1·90	7·28	8·82	10·18	5·34
	100·03	100·00	100·18	100·00	100·00	100·00	100·00
Potassium in carbonate,	43·85	40·39	46·61	41·93	39·39	28·77	21·86
Equal to potash (K_2O),	52·82	48·65	56·15	50·51	47·45	34·65	26·33
Potassium in hydrate,	—	—	—	—	—	—	—
Equal to potash,	—	—	—	—	—	—	—
Potassium in sulphate,	5·23	6·45	4·43	6·05	6·33	7·83	17·43
Equal to potash,	6·30	7·77	5·33	7·28	7·62	9·44	21·00
Potassium in chloride,	1·39	1·91	·54	·43	1·09	3·04	4·80
Equal to potash,	1·66	2·30	·66	·51	1·31	3·66	5·78
Total potassium,	50·47	48·75	51·58	48·41	46·81	39·64	44·09
Equal to potash,	60·78	58·72	62·14	58·30	56·38	47·75	53·11
Total available potassium,	43·85	40·39	46·61	41·93	39·39	28·77	21·86
Equal to potash,	52·82	48·65	56·15	50·51	47·45	34·65	26·33
Or carbonate of potassium,	77·50	71·38	82·38	74·10	69·61	50·84	38·63
Total alkali calculated as potash,	55·09	50·70	60·00	53·18	50·19	45·43	30·03
Ratio of sodium to available potassium —potassium, 100,	2·66	2·47	4·04	3·11	3·40	18·31	8·27
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100,	2·97	2·77	4·52	3·48	3·81	20·49	9·26
Analyst,	TATLOCK.	PESIER.	TATLOCK.	PESIER.	PESIER.	BASTELAER	PESIER.

It will be observed that the American pot-ashes contain a large proportion of hydrate or caustic potash. This occurs as a result of the use of lime in lixiviating the wood ashes, which not only causticises a portion of the carbonate, but renders soluble a certain amount of potash which would otherwise remain combined with silica in the insoluble matter. It is plain that for equal strengths there must be an advantage, for soap-making purposes, in the use of a product which contains a large proportion of caustic; as not only is lime thereby saved in the causticising, but a smaller precipitate of carbonate of calcium is obtained than would otherwise be the case, the washing of which is always tedious—not to speak of the loss in potash retained by the latter.

Although the manufacture of commercial carbonate of potassium from wood ashes has, for various reasons, fallen off to a large extent of late years, the amount made from this source in America and the countries of Europe is not less than 20,000 tons per annum, representing, even at present low prices, a total money value of about £400,000. Of this quantity one-half is produced in America. About 4000 tons were delivered from the inspection stores of Montreal alone in 1877.

2. *From Beet-root Molasses.*—A comparatively large proportion of potassium exists in the juice of beet-root, chiefly in the form of nitrate, which is for the most part left in the molasses or mother liquor remaining after the extraction of the sugar by crystallization. The following is a statement by Ritthausen of the composition of sugar beet:—

	Per Cent.
Sugar,	11·213
Cellulose,	1·364
Protein compounds,	·846
Other organic matters,	3·864
Ash,	·944
Water,	81·769
	100·00

The following is an analysis, by Eylerts, of the whole ash of the sugar beet:—

	Per Cent.
Potash,	42·50
Soda,	16·01
Lime,	4·23
Magnesia,	2·53
Oxide of iron,	·23
Alumina,	·28
Phosphoric acid,	3·77
Sulphuric acid,	1·84
Silicic acid,	·58
Chlorine,	2·15
Carbonic acid,	25·36
	99·48

The subjoined table (XI.) shows the composition of some samples of the beet-root molasses:—

TABLE XI.

	1.	2.	3.	4.	5.
Water,	15·2	18·0	18·5	19·0	19·7
Sugar,	49·0	48·0	50·7	46·9	49·8
Salts and organic matter,	35·8	34·0	30·8	34·1	30·5
	100·0	100·0	100·0	100·0	100·0
Analyst,	Brünner.	Frioke.	Lunge.	Heidenpriern.	

The percentage composition of the ash of the molasses, according to Heidenpriern, is stated in the subjoined table:—

TABLE XII.

	1.	2.	3.
Potash,	51·72	50·38	47·67
Soda,	8·00	8·29	11·43
Lime,	5·04	3·12	3·60
Magnesia,	·18	·18	·10
Carbonic acid,	28·90	28·70	27·94
Sulphuric acid, Phosphoric acid, Silicic acid, Chlorine, Oxide of iron,	6·16	9·33	9·26
	100·00	100·00	100·00

The molasses are diluted with water, fermented by addition of yeast, and the spirit distilled off. The residual fluid, or "vinasse," which has a specific gravity of about 1·028, is neutralized with chalk, which is even added in excess, concentrated, and the sulphate of calcium allowed to deposit. The clear but dark-coloured liquor is then run from a pipe, in a continuous stream, into iron pans, 50 feet in length, 5 feet in width, and 15 inches deep, and evaporated by surface heat until the portion nearest to the furnace takes fire and burns to a carbonaceous ash, care being taken to regulate the heat so that the sulphates will not be reduced to sulphites, thio-sulphates, and sulphides. In some districts the carbonized ash is raked out, and allowed to burn in heaps in the air. The cinder thus obtained, termed "salin" or "schlempekohle," varies in composition according to the soil on which the beet has been grown, the potassium being sometimes largely replaced by sodium, particularly where much of the natural potash has been abstracted from the soil by successive crops, and has not been replaced. The following table (XIII.) shows, according to Grüneberg, the average composition of the schlempekohle thus obtained:—

TABLE XIII.

	Per Cent.
Carbonate of potassium,	30 to 35
Sulphate of potassium,	6 to 8
Chloride of potassium,	18 to 22
Carbonate of sodium,	18 to 20
Insoluble,	28 to 15
	100 100

Formerly a considerable proportion of this product was sold for the local manufacture of saltpetre by double decomposition with nitrate of sodium (Chili saltpetre); but now it is, for the most part, refined, a carbonate of high strength being produced. This is done by lixiviating with several successive waters, the liquors in some cases being merely evaporated to dryness and the residue calcined, whereby a carbonate of low quality is produced, of which the following is an analysis by Ducastel:—

	Per Cent.
Carbonate of potassium,	67·20
Sulphate of potassium,	2·91
Chloride of potassium,	26·09
Carbonate of sodium,	3·80
	100·00

More commonly, however, the lixivium, which should have a specific gravity of about 1·230, is concentrated by waste heat, during which sulphate and chloride of potassium, as well as a mixture of these, known as "mixed salts," crystallize out, while the mother liquor is evaporated to dryness, and carefully calcined on a reverberatory hearth. When much carbonate of sodium is present, the last liquors, instead of being brought to dryness, are boiled down till they show a density of about 1·55, and run into coolers, when a double salt, having the composition $K_2CO_3.Na_2CO_3 + 12H_2O$, crystallizes out. The mother liquor from this, containing but little soda, is boiled to dryness and the product calcined, yielding a rich and pure carbonate. The double salt is further treated by digesting with a small quantity of warm water, which leaves the greater part of the carbonate of sodium insoluble, the strong lye from which, being evaporated to dryness and roasted, yields a further quantity of good commercial carbonate of potassium. The following table (XIV.) shows the composition of some samples, analyzed by TATLOCK, of beet-root carbonate thus made, representing lots delivered in this country:—

TABLE XIV.

	1	2	3	4
Carbonate of potassium,	92·68	91·22	90·83	90·25
Sulphate of potassium,	·43	2·76	2·67	3·81
Chloride of potassium,	2·45	1·92	2·52	2·92
Carbonate of sodium,	3·98	2·99	2·68	2·52
Soluble silica and alumina,	—	—	—	—
Insoluble matter,	·06	·08	·27	·21
Water,	·50	·85	·90	·45
	100·00	99·82	99·87	100·16
Potassium in carbonate,	52·44	51·62	51·39	51·06
Equal to potash (K_2O),	63·17	62·17	61·91	61·52
Potassium in sulphate,	·19	1·24	1·20	1·71
Equal to potash,	·23	1·49	1·44	2·06
Potassium in chloride,	1·29	1·01	1·32	1·53
Equal to potash,	1·55	1·22	1·59	1·84
Total potassium,	53·92	53·87	53·91	54·30
Equal to potash,	64·95	64·88	64·94	65·42
Total alkali calculated as potash,	66·70	64·83	64·29	63·76
Ratio of sodium to available potassium — potassium, 100,	3·29	2·51	2·26	2·14
Ratio of soda (Na_2O) to available potash (K_2O) — potash, 100,	3·68	2·81	2·53	2·39

It is of course impossible to obtain samples of the product at all stages of the manufacture, from the beet to the finished carbonate as the sugar manufacturer does not produce the latter, but disposes of the molasses to the distiller, who mixes them with others from different works, and which may be derived from other beets. It is thus difficult, on account of this mixing of molasses from various sources, to obtain samples representing the consecutive stages of the manufacture, when only the one kind or quality of the material has been operated upon. It would be desirable, however, to procure a complete set of analyses of several different kinds of beet, and all the products prepared from them, without admixture of any other variety at any stage of the process.

It has been proposed to boil down and crystallize saltpetre from the molasses *directly;* but this does not seem to have been caried out. By the process of DUNCAN and NEWLANDS, however, a large proportion of the potash present in the molasses obtained in the refining of beet sugar is recovered in the form of potash alum, by treatment of the syrups with sulphate of aluminium. (See ALUM.)

In France, Germany, Belgium, and Austria, about 12,000 tons per annum of carbonate are at present made from beet alone, and the manufacture is probably increasing. It is very questionable whether it is a wise policy to withdraw from the soil so much of the potash, which is so essential to the growth of the beet, especially as it ought to be restored in some form; the only advantage gained being that the greater part of it is recovered in the state of carbonate, which brings a higher price than the sulphate and chloride—these being the forms in which it is usually restored to the soil as manure.

3. *From Suint.*—The wool of sheep contains a large proportion (frequently about a third of its weight) of a peculiar organic compound of potassium, usually called "sudorate" or "suintate." This substance is exuded from the skin, the potassium being derived from the herbs and grasses on which the animals feed. The following is an analysis, by TATLOCK, of this substance:—

		Per Cent
Combined with organic matter	Potash,	24·76
	Soda,	1·49
	Lime,	·89
	Sulphate of potassium,	2·83
	Chloride of potassium,	3·44
	Silica,	·15
	Organic matters,	44·04
	Water,	22·40
		100·00

This substance was investigated by VAUQUELIN and CHEVREUL, and the method of obtaining carbonate of potassium from it was perfected by MAUMENE and ROGELET.

The following is the process generally followed:—The wool is pressed into casks and there exhausted with several successive quantities of cold water, which gives a brown solution of spec. grav. 1·1. This is evaporated to dryness, and the residue calcined in iron retorts, by which illuminating gas is obtained; and the charcoal or cinder which is left is lixiviated, the liquor concentrated, during which sulphate and chloride of potassium separate, and the strong lye ultimately evaporated to dryness and calcined, when the carbonate is obtained of a fine white colour. It is commonly stated that this product is free from soda, but this is erroneous; as will be seen, not only from the composition of the suint itself, as given above, but also from the following analyses (Table XV.), made by the same chemist, of the carbonate itself:—

TABLE XV.

	First Quality.		Second Quality.
	1.	2.	3.
Carbonate of potassium,	91·20	89·41	80·57
Sulphate of potassium,	·52	·17	4·75
Chloride of potassium,	1·97	1·67	4·51
Carbonate of sodium,	4·39	3·83	2·48
Insoluble,	·04	·06	·30
Water,	1·60	4·70	7·25
	99·72	99·84	99·86
Potassium in carbonate,	51·60	50·59	45·59
Equal to potash (K_2O),	62·17	60·94	54·92
Potassium in sulphate,	·23	·07	2·13
Equal to potash,	·28	·09	2·57
Potassium in chloride,	1·03	·88	2·36
Equal to potash,	1·24	1·05	2·84
Total potassium,	52·86	51·54	50·08
Equal to potash,	63·69	62·08	60·33
Total alkali calculated as potash,	66·08	64·34	57·12
Ratio of sodium to available potassium—potassium, 100,	3·69	3·28	2·36
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100,	4·13	3·67	2·64

A refined carbonate is now made, however, from this source, of even higher quality than the above, by removing the neutral salts and carbonate of sodium during evaporation.

The principal seats of the manufacture of this variety of carbonate are Rheims, Elbœuf, Fourmies, and Verviers; and in all, about 1000 tons per annum are at present made. According to WAGNER, there were imported in 1868 into the United Kingdom 62,000 tons of wool from Australia and the Cape, containing about one-third of its weight of "suint," from which 7000 to 8000 tons of carbonate of potassium might have been made, representing a money value of about £260,000; yet none of this was recovered in this country.

4. *From the Sulphate by Le Blanc's Process.*—This method is essentially the same in principle as that followed in the manufacture of carbonate of sodium (soda ash) from the corresponding sulphate of sodium (salt cake). The sulphate of potassium employed may have been obtained either by the treatment, with sulphuric acid, of commercial chloride of potassium, or by the double decomposition of the latter with sulphate of magnesium (kieserit); or it may have been procured from beet-root. The sulphate is mixed with about an equal weight of broken-down limestone and about two-thirds of its weight of coal, and the mixture calcined in an ordinary soda ash furnace; the process not differing materially from that followed in the preparation of "black ash" or "ball soda." The limestone used must be very pure, and the coal should be as free as possible from ash, as otherwise silica and alumina are introduced, which combine with and retain a portion of the potash. The ash thus obtained is lixiviated with several successive waters, which dissolve out the soluble salts of potassium and sodium, leaving a large amount of insoluble matter, or "potash waste," of which the following is an analysis:—

	Per Cent.
Carbonate of calcium,	17·40
Sulphate of calcium,	1·75
Thiosulphate of calcium,	10·16
Sulphide of calcium,	·87
Oxysulphide of calcium,	34·23
Carbonate of magnesium,	1·49
Carbonate of potassium,	·70
Carbonate of sodium,	·29
Oxide of iron,	·54
Alumina,	1·46
Silica,	5·20
Carbon,	4·40
Water,	21·51
	100·00

If the product is to be employed only in the manufacture of other potassium salts, the liquor is evaporated to dryness, and the result calcined. The following table (XVI.) of analyses, according to TATLOCK, shows the composition of the crude carbonate thus obtained:—

TABLE XVI.

	1.	2.	3.	4.	5.	6.
Carbonate of potassium,	70·67	71·92	71·17	75·79	63·13	59·36
Hydrate of potassium,	11·33	7·71	6·37	—	5·96	5·80
Sulphate of potassium,	6·27	8·21	8·15	8·14	8·58	13·61
Chloride of potassium,	1·81	2·80	2·59	4·20	5·82	2·71
Sulphite of potassium,	1·31	1·85	·64	4·59	7·07	5·36
Thiosulphate of potassium,	·81	·39	1·36	·77	2·14	1·22
Sulphide of potassium,	trace.	trace.	trace.	1·06	·17	·79
Carbonate of sodium,	—	—	—	·79	—	—
Hydrate of sodium,	1·79	1·96	1·90	1·43	3·67	3·20
Soluble silica and alumina,	·48	·53	·50	—	·50	—
Insoluble matter,	1·69	1·99	2·27	·20	1·72	·97
Water,	3·45	2·39	4·75	3·27	1·30	7·00
	99·61	99·75	99·70	100·24	100·06	100·02
Total potassium,	52·63	52·29	50·59	52·06	51·27	48·86
Equal to potash (K_2O),	63·40	62·99	60·94	62·72	61·76	58·86
Total available potassium,	47·89	46·07	44·71	42·88	39·88	37·63
Equal to potash,	57·69	55·50	53·86	51 66	48·04	45·33
Or carbonate of potassium,	84·63	81·42	79·00	75·79	70·47	66·50
Total alkali calculated as potash,	59·79	57·80	56·09	54·05	52·26	49·10
Ratio of sodium to available potassium—potassium, 100,	2·15	2·44	2·44	2·71	5·29	4·89
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100,	2·40	2·73	2·73	3·04	5·92	5·47

If the article is intended for the market, however, other treatment of the lixivium is necessary. It is concentrated in ordinary round-bottomed pans, and the sulphate and chloride of potassium and carbonate of sodium fished out during the evaporation; the strong liquor is then ladled or run off, and if it is not desired to make caustic potash, it is then mixed with sawdust and gently calcined on a reverberatory brick hearth having a solid bed, during which it is carefully turned over, by raking, to equalize the heat and action. The object of the last operation is not only to carbonate all the hydrates, but to destroy the sulphites, thiosulphates, and sulphides, and to convert them either into sulphate or carbonate. The result is a commercial carbonate of potassium of comparatively high strength, of which the following are TATLOCK's analyses (Table XVII.), representing the article made both in this country and on the Continent:—

TABLE XVII.

	1.	2.	3.	4.
Carbonate of potassium,	92·19	91·25	88·89	88·64
Sulphate of potassium,	3·94	1·04	3·57	7·36
Chloride of potassium,	1·49	2·99	1·96	2·54
Carbonate of sodium,	1·43	1·8	4·00	1·17
Soluble silica and alumina,	·13	·30	·16	·13
Insoluble matter,	·15	·22	·07	·11
Water,	·80	2·20	1·27	·33
	100·13	99·82	99·92	100·28
Potassium in carbonate,	52·16	51 64	50 30	50·15
Equal to potash (K_2O),	62·84	62·20	60·59	60·42
Potassium in sulphate,	1·77	·46	1·60	3·30
Equal to potash,	2·13	·56	1·93	3·98
Potassium in chloride,	·78	1·57	1·02	1·33
Equal to potash,	·94	1·89	1 23	1·60
Total potassium,	54·71	53·67	52·92	54·78
Equal to potash,	65·91	64·65	63·75	66·00
Total alkali calculated as potash,	64·11	63·81	64·14	61 46
Ratio of sodium to available potassium—Potassium, 100,	1·19	1·49	3 45	1·04
Ratio of soda (Na_2O) to available potash (K_2O)—Potash, 100,	1·33	1·70	3·84	1·16

There is every prospect that carbonate from this source will soon be made not only at a cheaper rate, but of even greater strength and purity than at present. At the works of Messrs. VORSTER & GRUENEBERG at Kalk, near Cologne, and of the Greenbank Alkali Co., St. Helens, Lancashire, carbonate of a high degree of strength and purity is made by this process.

A very fine hydrated carbonate of potassium, pure white in colour, and granulated, is made by boiling down the liquors obtained by lixiviating the ash, after calcining with sawdust, to such an extent that the whole product does not contain more than from 15 to 18 per cent. of water, drawing the fire, and stirring during the cooling, by which the carbonate is obtained in the state of fine grains like gunpowder, but snow-white in colour. The following table (XVIII.) gives analyses, by TATLOCK, of this granulated carbonate:—

TABLE XVIII.

	1.	2.	3.	4.
Carbonate of potassium,	78·24	77·98	77·87	77·46
Sulphate of potassium,	·30	·59	·37	·06
Chloride of potassium,	2·06	2·60	1·57	2·20
Carbonate of sodium,	3·44	3·00	4·20	2·86
Soluble silica and alumina,	—	·50	—	—
Insoluble matter,	·03	·06	·02	·04
Water,	15·85	15·10	15·85	17·19
	99·92	99·83	99·88	99·81
Potassium in carbonate,	44·27	44·12	44·06	43·83
Equal to potash (K_2O),	53·33	53·15	53·08	52·80
Potassium in sulphate,	·13	·27	·18	·02
Equal to potash,	·16	·32	·21	·03
Potassium in chloride,	1·08	1·36	·82	1·15
Equal to potash,	1·30	1·63	·99	1·38
Total potassium,	45·48	45·75	45·06	45·00
Equal to potash,	54·79	55·10	54·28	54·21
Total alkali calculated as potash,	56·38	55·81	56·81	55·34
Ratio of sodium to available potassium—potassium, 100,	3·37	2·95	4·29	2·81
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100,	3·77	3·29	4·62	3·16

The carbonate of potassium and water approximately correspond to the formula $K_2CO_3 + 2H_2O$. This article is manufactured of great purity at the works of the North British Chemical Co., Dalmuir, near Glasgow.

The loss by volatilization, and by the formation of insoluble potassium compounds in the furnace operations, is very considerable; and hence the value of carbonate of potassium is higher, in proportion to the cost of the materials used and the labour expended, than the corresponding carbonate of sodium made by LE BLANC's process. It should be noted that there is not necessarily any difference, as regards strength and purity, between the carbonates obtained respectively from wood ashes, beet-root, suint, and sulphate or chloride of potassium; this being merely a question of the extent to which the refining is carried. It must be easier, however, to remove chloride of sodium from chloride of potassium by washing, than to separate carbonate of sodium from carbonate of potassium by any process of refining.

About 15,000 tons of carbonate of potassium are made on the Continent and in the United Kingdom by LE BLANC'S process, exclusive of the amount produced, for their own use, by manufacturers of bichromate, ferrocyanide, and other special potassium salts.

It is quite plain that carbonate of potassium, and even caustic potash, prepared from any of these sources, must contain, in the form of hydrate or carbonate, a large proportion of the sodium originally present in the raw materials used; and for this reason the process of "alkalimetry," or neutralization of the alkali by a dilute acid of known strength, is worthless for determining the true value of these substances—the whole of the soda being thereby estimated as potash; and not only so, but from the fact that soda has a lower atomic weight than potash,

in the proportion of 1 to 1·52, for every part of soda present a quantity of the standard acid would be consumed representing 1½ part of potash, thus magnifying the error. Nothing short of a determination of the respective proportions of all the soluble salts present can correctly represent the composition and value of these products, or even show the amount of available potash they contain. This becomes all the more important when we consider that the presence of comparatively small quantities of soda are objectionable for many purposes. For instance, in the manufacture of soft soap its presence in a greater ratio than that of 4 of sodium to 100 of available potassium is apt to produce sufficient opaque soda soap to destroy the required transparency of the product; and for the preparation of certain potassium salts, such as ferrocyanide or bichromate, it is very undesirable to have sodium present in larger proportion than 2 parts to 100 of available potassium, on account of the trouble caused by the accumulation and crystallization of its salts in the liquors.

Carbonate of potassium is sometimes formed during the reduction of iron ores in the blast furnace, and exudes from the walls of the latter at a point immediately above the tuyeres. It is often of great purity, but it is generally associated with cyanide of potassium. The coal and ores employed frequently contain a minute quantity of potassium compounds, and are thus the source of this carbonate. Although it sometimes does not appear, a single furnace will occasionally yield 10 or 15 cwts. in a year. The following is an analysis, made by TATLOCK, of a sample of this substance obtained from one of the blast furnaces of Ardeer Iron Works, Ayrshire :—

	Per Cent.
Carbonate of potassium,	85·64
Sulphate of potassium,	·23
Chloride of potassium,	·35
Cyanide of potassium,	·13
Carbonate of sodium,	5·31
Soluble silica and alumina,	·24
Insoluble matter,	.04
Water,	7·92
	99·86

Applications.—Commercial carbonate of potassium is largely consumed in making caustic potash for soft soap purposes, and also for the manufacture of bichromate and ferrocyanide of potassium; and it is employed on a considerable scale for producing the emulsion with olive oil used in the preparation of cotton cloth for Turkey red. Much of it is also used in the composition of soluble and insoluble potash glass; for general cleansing and scouring purposes; and in medicine its dilute solution is prescribed as an antacid and diuretic.

Properties.—Pure anhydrous carbonate of potassium is a hard white solid, of spec. grav. 2·207, having a strong alkaline reaction and taste. It crystallizes from a highly concentrated hot solution in the form of rhombic octahedra, which have the composition $K_2CO_3,2H_2O$. It melts at a full red heat, and at a higher temperature slowly volatilizes. At ordinary temperatures it is decomposed by all dilute acids, with effervescence due to the liberation of carbonic anhydride, a potassium salt of the acid employed being formed. In moist air it is highly deliquescent, dissolving in the water thus absorbed, and gradually passes into the bicarbonate. It dissolves with evolution of heat in rather less than its own weight of water, according to GERLACH, whose table (XIX.) of the proportions dissolved at 15° C., corresponding to various specific gravities, is subjoined:—

TABLE XIX.

Specific Gravity.	K_2CO_3, Per Cent.	Specific Gravity.	K_2CO_3, Per Cent.
1·00914	1	1·27893	28
1·01829	2	1·28999	29
1·02743	3	1·30105	30
1·03658	4	1·31261	31
1·04572	5	1·32417	32
1·05513	6	1·33573	33
1·06454	7	1·34729	34
1·07396	8	1·35885	35
1·08337	9	1·37082	36
1·09278	10	1·38279	37
1·10258	11	1·39476	38
1·11238	12	1·40673	39
1·12219	13	1·41870	40
1·13199	14	1·43104	41
1·14179	15	1·44338	42
1·15200	16	1·45573	43
1·16222	17	1·46807	44
1·17243	18	1·48041	45
1·18265	19	1·49314	46
1·19286	20	1·50588	47
1·20344	21	1·51861	48
1·21402	22	1·53135	49
1·22459	23	1·54408	50
1·23517	24	1·55728	51
1·24575	25	1·57048	52
1·25681	26	1·57079	52·024
1·26787	27		

The solution mentioned last on the table, which is saturated, boils at 113° C.

BICARBONATE OF POTASSIUM ($KHCO_3$). Synonyms—Bicarbonate of Potash, Acid Carbonate of Potash, Potassium Hydrocarbonate; *Bicarbonate de Potasse*, French; *Zweifach Kohlensaures Kali*, German.

Preparation.—1. By passing carbonic anhydride through solution of pure hydrate of potassium in 80 per cent. alcohol, pouring off the clear fluid, continuing the passage of the gas, and washing the crystals with fresh alcohol (PESCI). 2. By mixing strong aqueous solutions of sesquicarbonate of ammonium and pure monocarbonate of potassium, filtering off the precipitated bicarbonate, and washing with cold water.

Manufacture.—For commercial purposes it is obtained by passing carbonic anhydride gas through a saturated solution of the ordinary carbonate, the substance being thrown down in the form of a white crystalline powder, which is then dissolved in the same solution by blowing in steam, taking care not to raise the temperature so high as to decompose the product. The liquor deposits tolerably large and well-formed crystals of bicarbonate on standing, and is separated by draining. The crystals are then dried at a moderate heat. The whole operation is conducted in lead vessels, and the carbonic anhydride gas is obtained by the decomposition of limestone with hydrochloric acid.

Properties.—Bicarbonate of potassium crystallizes in the form of rhomboidal prisms of the monoclinic system. It is not nearly so soluble in water as the monocarbonate; and its aqueous solution has an alkaline reaction, and a cooling and alkaline taste. The following table (XX.), by POGGIALE, shows its solubility in water at different temperatures:—

TABLE XX.

At	0° C.,	100 parts water	dissolve	19·61 parts.
"	10°	"	"	23·33 "
"	20°	"	"	26·91 "
"	50°	"	"	37·92 "
"	60°	"	"	41·35 "
"	70°	"	"	45·24 "

The solution when boiled slowly gives off carbonic acid gas, the monocarbonate alone finally remaining dissolved. It is soluble in 1200 times its weight of alcohol. It can readily be obtained in a state of great purity, and is largely used in medicine as an antacid and diuretic, and in cases of gout and lithic acid calculus.

CHLORIDE OF POTASSIUM, KCl. Synonyms, Muriate of Potash; German, *Chlorkalium;* French, *Chlorure de Potassium.*—This salt is found in sea water, in the ashes of plants, and in the mineral deposits at Stassfurt and Kalutz. In the pure state it is called Sylvine.

Properties.—Chloride of potassium crystallizes in colourless cubes, which decrepitate when heated, and are more volatile than chloride of sodium. It is slightly soluble in alcohol, and much less soluble in dilute hydrochloric acid than in water.

GERLACH's table (XXI.), showing the quantities of chloride of potassium in aqueous solutions of different densities at 59° Fahr., or 15° C. is here given.

TABLE XXI.

Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.
1	1·00651	13	1·08654
2	1·01300	14	1·09345
3	1·01950	15	1·10036
4	1·02600	16	1·10750
5	1·03250	17	1·11465
6	1·03916	18	1·12179
7	1·04582	19	1·12894
8	1·05248	20	1·13608
9	1·05914	21	1·14348
10	1·06580	22	1·15088
11	1·07271	23	1·15828
12	1·07962	24	1·16568

24·9 per cent. = 1·17234.

SCHIFF's table (XXII.) of the quantity of chloride of potassium in aqueous solutions of different densities, at 17°·5 C.

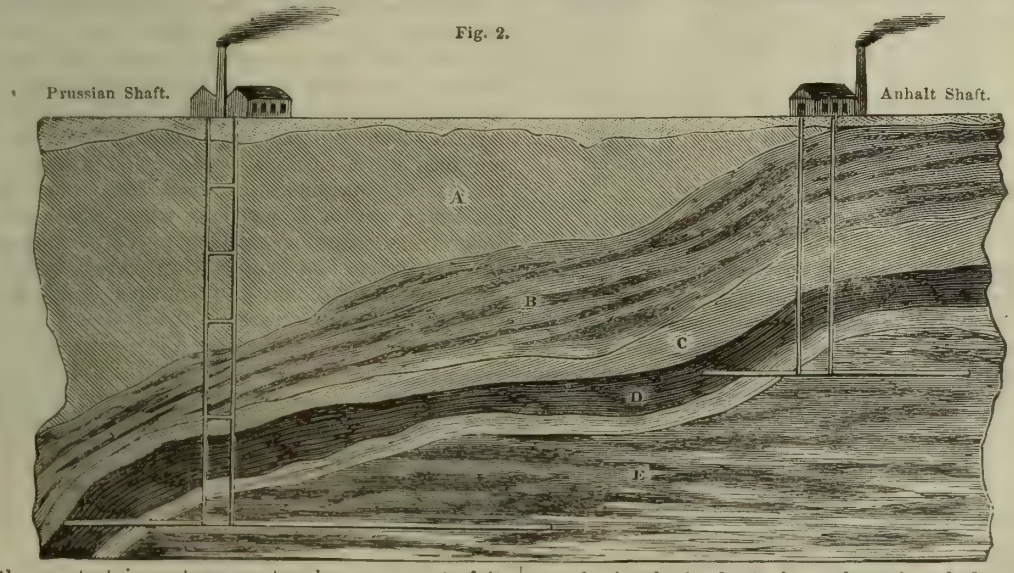
TABLE XXII.

Specific Gravity.	Per Cent. of KCl.	Specific Gravity.	Per Cent. of KCl.
1·0062	1	1·0866	13
1·0125	2	1·0937	14
1·0189	3	1·1008	15
1·0254	4	1·1080	16
1·0319	5	1·1152	17
1·0385	6	1·1225	18
1·0451	7	1·1298	19
1·0518	8	1·1372	20
1·0586	9	1·1446	21
1·0655	10	1·1521	22
1·0725	11	1·1597	23
1·0795	12	1·1673	24

Uses.—Chloride of potassium is extensively used in the manufacture of saltpetre, alum, chlorate of potash, and sulphate of potash. It is also a valuable constituent of manures, and it enters into the composition of certain freezing mixtures.

Chloride of potassium, or as it is more commonly called, commercially, muriate of potash, is a salt of the greatest importance, not only on account of its direct applications, but also because of the extent to which it is applied in the preparation of the other salts of potassium.

Fig. 2.



Commercial chloride of potassium, or muriate of potash, is obtained—1, from the mineral deposits at Stassfurt and Kalutz; 2, from kelp; 3, from the mother liquors of sea water; and 4, as a bye product in the manufacture of carbonate of potash from beet-root.

Extraction of Chloride of Potassium from the Mineral Deposits at Stassfurt and Kalutz.—In the neighbourhood of Stassfurt, in the Prussian province of Saxony, deposits of potash salts, called by the Germans *abraum*, or dung salt, have been found; and up to the present time three shafts have been sunk on these deposits—one by the Prussian Government at Stassfurt; another by the Duchy of Anhalt, opposite Stassfurt, at Leopoldshall; and a third by a Mr. DOUGLAS at Douglashall, which is situated about twelve miles north-east of Stassfurt. The potash salts found in these deposits consist principally of carnallit ($KCl,MgCl_2 + 6H_2O$) and kainit ($K_2SO_4MgSO_4MgCl_2 + 6H_2O$); but besides these considerable quantities of other valuable salts are obtained. From the accompanying section (Fig. 2—A, red sandstone; B, gypsum; C, marl; D, potash salts; E, rock salt) it will be observed that the potash salts are found above the rock salt, which has led to the belief that they have been formed by the gradual evaporation of a vast sea. The deposits vary, not only in thickness, but in the depth at which they are found. At Stassfurt the bed has an average thickness of about 160 feet, of which from 60 to 100 feet consist of carnallit, and it is found in the Prussian shaft at a depth of 840 feet, and in the Anhalt shaft at 492 feet. At Douglashall the deposit, which is about 400 feet from the surface, appears to be of much greater extent, as the shaft has already been sunk 430 feet on the carnallit bed without finding the bottom. The following are the quantities of crude carnallit worked up in the chemical factories at Stassfurt and Leopoldshall between 1863 and 1875:—

	Tons.
1863, in 11 chemical works,	64,400
1864, " 18 " "	138,750
1865, " 16 " "	95,000
1866, " 18 " "	172,600
1867, " 16 " "	167,500
1868, " 18 " "	201,650
1869, " 20 " "	230,000
1870, " 21 " "	312,200
1871, " 25 " "	403,200
1872, " 33 " "	514,200
1873, " 33 " "	452,350
1874, " 33 " "	426,790
1875, " 33 " "	494,414

Pure carnallit contains 26·88 per cent. of chloride of potassium; but the crude mineral, as extracted from the Stassfurt mines, contains on an average from 16 to 18 per cent. The following are analyses of average samples of Stassfurt and Douglashall deposits, and the theoretical composition of pure carnallit:—

	Stassfurt. (Frank.)	Douglashall. (Tatlock.)	Pure Carnallit.
	Per Cent.	Per Cent.	Per Cent.
Chloride of potassium,	16·00	17·00	26·88
Chloride of sodium,	21·40	20·26	—
Chloride of magnesium,	21·00	22·99	34·22
Sulphate of magnesium,	13·00	9·43	—
Sulphate of calcium,	1·20	·97	—
Insoluble,	2·10	1·56	—
Water,	25·30	27·79	38·90
	100·00	100·00	100·00

The extraction of chloride of potassium from the Stassfurt deposit was begun in 1861 by one small work, and developed so rapidly that, in 1872, there were thirty-three works operating on about 500,000 tons of the raw material, and turning out about 60,000 tons of muriate of potash, containing from 80 to 98 per cent. of chloride of potassium. The extraction of the chloride of potassium from the carnallit depends on the fact that the double salt only separates from solutions containing an excess of chloride of magnesium. The carnallit is dissolved in water with the aid of steam; and when it has acquired the proper degree of concentration (32° B. or 53° Twd.), a crop of impure chloride of potassium crystals is obtained on cooling, the strength of which can be increased by repeatedly digesting with cold water. The effect produced by washing the impure chloride of potassium with cold water may be seen in the following analyses by G. KRAUSE:—

	Unwashed.	After First Washing.	After Second Washing.
	Per Cent.	Per Cent.	Per Cent.
Chloride of potassium,	58·24	62·82	80·61
Chloride of sodium,	21·80	18·42	9·97
Chloride of magnesium,	4·75	1·10	·04
Sulphate of magnesium,	1·46	·70	·66
Water,	13·75	16·96	8 72
	100·00	100·00	100·00
Calculated free from water— Chloride of potassium,	67·52	75·65	88·31

The crystals are dried by centrifugal machines, and afterwards furnaced, by which means the water is reduced to about 1 per cent.

Instead of dissolving the crude carnallit in water, it may be treated with a hot concentrated solution of chloride of magnesium, which dissolves the carnallit, but very little salt or sulphate of magnesium. On cooling the carnallit crystallizes out, and the mother liquor can be used for treating a fresh quantity of the raw material. The carnallit crystals are then dissolved in hot water, and a crop of chloride of potassium is obtained, from which the impurities may be removed by washing with cold water. The following analyses, by TATLOCK, show the composition of a sample of crystallized sylvine, and of commercial chloride of potassium of different strengths, made from Stassfurt carnallit:—

	Sylvine.	Samples of Commercial Chloride of Potassium.			
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Chloride of potassium,	98·86	98·86	96·00	90·16	79·44
Sulphate of potassium,	—	·13	trace.	trace.	·05
Chloride of sodium,	—	·54	2·79	6·46	16 63
Sulphate of calcium,	·54	·12	·16	·07	·26
Chloride of magnesium,	·24	·24	·20	·19	·20
Insoluble,	·12	·16	·27	·14	35
Water,	·16	·13	·40	2 88	3·06
	99·92	100·10	99·81	99 90	99·99

The rapid development of the manufacture of chloride of potassium at Stassfurt led to the examination of other deposits of a similar character,

and the discovery, in 1868, of a deposit at Kalutz in Galicia, which, although of much smaller dimensions, was yet of sufficient importance to justify the establishment of works for the extraction of the chloride of potassium. At Kalutz, the chloride of potassium is found in considerable quantity as nearly pure sylvine, but the bulk is associated with salt, gypsum, and clay, and contains in the raw state from 22 to 24 per cent. of chloride of potassium. Owing to the absence of magnesium salts, the process for the extraction of the chloride of potassium is much simpler. It consists in heating the raw material with a saturated solution of chloride of potassium, which dissolves out the chloride of potassium from the mineral, and only a comparatively small quantity of salt; on cooling a crop of crystals of nearly pure chloride of potassium is obtained, and the mother liquor is used for the treatment of a fresh quantity of the raw material. The chloride of potassium from the deposit at Kalutz which finds its way into the English market is of the highest quality, as may be seen by the following analyses by Tatlock:—

	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Chloride of potassium,	99·24	98·72	98·42	97·82
Chloride of sodium,	·57	·30	1·08	1·45
Insoluble,	·10	·11	·10	·10
Water,	·13	·95	·25	·50
	100·04	100·08	99·85	99·87

II. *Extraction of Chloride of Potassium from Kelp.*—Kelp is the ash of certain kinds of sea weed, which in this country are collected chiefly in the western and northern islands of Scotland, and on the north-west coast of Ireland. Two kinds of kelp are carefully distinguished—namely, drift-weed kelp and cut-weed kelp. The former is the ash of the sea weed which is thrown upon the shore during storms, and is much richer in potash salts than the kelp made from the weed which is cut, as will be clearly seen from the following analyses of samples of each kind:

	Drift Weed. (Tatlock.)		Cut Weed. (Ogilvie.)	
	Per Cent.	Per Ton.	Per Cent.	Per Ton.
		Cwts. Lbs.		Cwts. Lbs.
Sulphate of potassium,	6·45	1 32·48	19·95	3 110·88
Chloride of potassium,	30·92	6 20·61	—	—
Sulphate of sodium,	1·75	39·20	3·10	69·44
Chloride of sodium,	13·23	2 72·35	15·67	3 15·01
Iodide of sodium,	·72	16·13	·15	3·36
Bromide of sodium,	trace.	trace.	trace.	trace.
Carbonate of sodium,	2·74	61·38	4·34	97·21
Hyposulphite of sodium,	·35	7·84	4·80	107·52
Sulphide of sodium,	·20	4·48	·49	10·97
Insoluble matter,	39·04	7 90·49	45·30	9 6·72
Water,	4·60	103·04	6·20	1 26·89
	100·00	20	100·00	20
Soluble salts,	56·36	11 30·47	48·50	9 78·39
Insoluble matter,	39·04	7 90·49	45·30	9 6·72
Water,	4·60	103·04	6·20	1 26·89
	100·00	20	100·00	20
Potash,	22·96	4 66·30	10·72	2 17·69
Iodine,	·61	13·66	·127	3·20

The extraction of chloride of potassium and the other valuable constituents of kelp is carried on in this country principally in the neighbourhood of Glasgow; but the number of works has greatly diminished during the last few years, owing principally to the discovery of the Stassfurt deposits. In 1854 there were nine establishments, whereas in 1877 there were only the three following:—Messrs. W. and M. Paterson, the North British Chemical Co., and Messrs. F. R. Hughes & Co.

The kelp is broken up into pieces about the size of road metal, and digested in a series of tanks, fitted with perforated false bottoms, till the gravity of the liquor is about 1·2. The liquor is then pumped into evaporating pans, and boiled down, the salt which separates during evaporation being fished out with a ladle. When the liquor has a gravity of about 1·3, it is run off into coolers, in which the chloride of potassium crystallizes out.

By evaporating the mother liquor still further, a second and third crop of crystals can be obtained. The strength of the chloride of potassium got in this way may be increased by washing with cold water. The following are Tatlock's analyses of samples of muriates of potash made from Scotch and French kelp:—

	From Scotch Kelp.		From French Kelp.	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Chloride of potassium,	89·55	86·67	90·05	86·43
Sulphate of potassium,	5·74	4·79	8·21	9·01
Chloride of sodium,	·62	3·19	·96	3·27
Carbonate of sodium,	·09	·26	·13	·17
Insoluble,	·20	·10	·25	·22
Water,	3·82	5·60	·50	1·00
	100·02	99·96	100·10	100·10

The average production of muriate of potash from kelp during the last ten years, in the neighbourhood of Glasgow, is estimated to be about 2500 tons annually.

III. *Extraction of Chloride of Potassium from the Mother Liquors of Sea Water.*—In the salt works on the south and west coasts of France, after the extraction of the salt, large quantities of mother liquors are obtained, consisting essentially of sulphate of magnesium, chloride of magnesium, chloride of potassium, and chloride of sodium; and from these liquors the sulphate of soda and chloride of potassium are extracted by Merle's process, which is known as the "méthode à vingt-huit dégrés."

The mother liquors are allowed to concentrate till they have acquired a specific gravity of 28° B. (45° Twd.), after which they are subjected, by means of Carré's ice machine, to 18° of cold, at which temperature a double decomposition takes place between the sulphate of magnesium and chloride of sodium, producing chloride of magnesium and sulphate of sodium, which crystallizes out as Glauber salt.

$$MgSO_4 + 2NaCl = MgCl_2 + Na_2SO_4.$$

The liquor from which the Glauber salt has been removed is then evaporated till it has a specific

gravity of 36° B. (62° Twd.), the salt which separates during evaporation being fished out; and upon cooling, the chloride of potassium crystallizes in the form of the double chloride of potassium and magnesium (artificial carnallit). The double salt is then washed with cold water, to decompose it into chloride of magnesium, which dissolves, and chloride of potassium, which remains in the solid state. The annual production of chloride of potassium from this source is said to amount to about 1000 tons.

IV. A considerable quantity of chloride of potassium is also obtained as a bye product from beet-root. The carbonaceous mass (schlempekohle) produced by the calcination of the refuse of the beet molasses from the distilleries contains, in addition to carbonate of potassium and other salts, about 20 per cent. of chloride of potassium; and when the liquor obtained by lixiviating the mass with water is evaporated to the proper degree of concentration, and allowed to cool, it deposits chloride of potassium, which may be freed from the greater part of the salts with which it is mixed by washing with cold water. The following are analyses of samples of beet-root muriate by CLARK :—

	Per Cent.	Per Cent.
Chloride of potassium,	77·35	74·50
Sulphate of potassium,	12·63	13·05
Carbonate of potassium,	1·79	4·09
Carbonate of sodium,	1·62	1·87
Cyanides,	trace	trace
Insoluble	·13	·25
Water,	6·40	6·20
Total,	99·92	99·96

POTASSIUM SULPHATE, K_2SO_4. Synonyms, Sulphate of Potash; German, *Schwefelsaures Kali;* French, *Sulphate de Potasse.*—This salt crystallizes in hard colourless six-sided prisms, which are insoluble in alcohol, and difficultly soluble in water. The crystals contain no combined water; but when heated they decrepitate, owing to the presence of a small quantity of mother liquor in the crystal.

BRANDE'S AND FIRNHABER'S TABLE (XXIII.) OF THE SOLUBILITY OF SULPHATE OF POTASH.

TABLE XXIII.

1 Part of Salt Soluble in	Temperature.	1 Part of Salt Soluble in	Temperature.
Parts of Water.	Degrees C.	Parts of Water.	Degrees C.
9·96	12·5	4·4	56·25
9·60	15·0	4·5	68·75
6·80	31·25	4·0	87·50
5·84	37·5	3·7	100
4·00	50		

Or,

100 Parts of Water at	Dissolve Parts of Salt.	100 Parts of Water at	Dissolve Parts of Salt.
Degrees C.		Degrees C.	
12·5	10	56·25	22
15	10·38	68·75	21·95
31·25	14	87·50	25
37·5	17	100	26
50	25		

Or,

Aqueous Solution Saturated at	Contains Per Cent. of Salt.	Aqueous Solution Saturated at	Contains Per Cent. of Salt.
12°·5 C.	9·125	56°·25 C.	18·500
15	9·400	68·75	18·000
31·25	12·812	87·5	20·000
37·5	14·600	100	21·100
50	20·000		

GERLACH'S TABLE (XXIV.) OF THE QUANTITY OF SULPHATE OF POTASH IN SOLUTIONS OF DIFFERENT DENSITIES AT 59° FAHR. OR 15° C.

TABLE XXIV.

Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.
1	1·00820	6	1·04947
2	1·01635	7	1·05790
3	1·02450	8	1·06644
4	1·03277	9	1·07499
5	1·04105		

9·92 per cent. = 1·08305.

It is largely used in the manufacture of alum, glass, carbonate of potash, and as a manure. Most of the sulphate of potash of commerce is made by the action of sulphuric acid on chloride of potassium; but considerable quantities are also extracted from kelp and beet-root.

The formation of sulphate of potash by the action of sulphuric acid on chloride of potassium is conducted in an ordinary salt cake furnace. The chloride of potassium is introduced into a metal decomposing pot, with the proper proportion of acid, and heated till it has acquired sufficient consistency, when it is transferred to a reverberatory furnace, and stirred with long iron paddles till the decomposition has been completely effected. Recently (1875), a furnace has been patented by Messrs. JONES and WALSH, in which the decomposition and calcination are conducted in the same vessel.

The chloride of potassium is introduced into a flat-bottomed circular metal pan, *a*, which forms the bed of the furnace (Fig. 3); and after the addition of the proper proportion of sulphuric acid, the rotating arms and rakes, which are made to revolve by suitable driving gear, are set in motion, and continue to revolve till the process of calcination is complete—the charge being heated by the flames from the fire, *b*, which passes over the surface of the pan, and is regulated by a damper. The following are analyses of samples of sulphate of potash thus made:—

	CLARK. Per Cent.		TATLOCK. Per Cent.
Sulphate of potassium,	91·15	....	93·94
Chloride of potassium,	1·11	....	·97
Sulphate of sodium,	2·34	....	2·20
Chloride of sodium,	·03	....	·03
Sulphate of calcium,	·57	....	·51
Sulphate of magnesium,	·48	....	·54
Sulphate of iron	·88	....	·57
Sulphuric acid,	2·28	....	1·02
Insoluble,	·94	....	·26
Water,	·17	....	·08
	99·95	....	100·12

Sulphate of potassium may also be made, as FRANK has shown, by the decomposition of kieserit ($MgSO_4 + H_2O$), a native sulphate of magnesium

found in large quantity at Stassfurt, with chloride of potassium. The process consists—1st., In the formation of a double sulphate of potassium and magnesium by the action of a hot solution of sulphate of magnesium (kieserit) on chloride of potassium.

$$3KCl + 2MgSO_4 = MgSO_4 + K_2SO_4 + KCl,MgCl_2$$

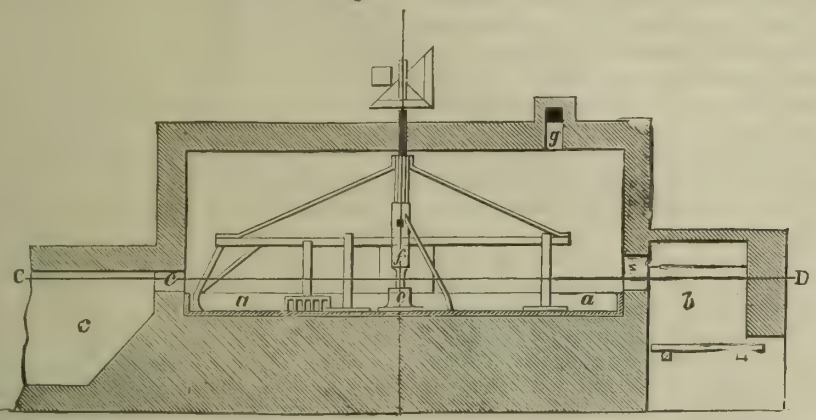
2nd. The decomposition of the double sulphate by means of a hot solution of chloride of potassium.

$$K_2SO_4,MgSO_4 + 3KCl = 2K_2SO_4 + KCl,MgCl_2$$

3rd. The decomposition of the artificial carnallit ($KCl,MgCl_2$) thus produced, with cold water, into chloride of magnesium, which dissolves, and chloride of potassium, which can be used over again.

During the evaporation of kelp liquor an impure sulphate of potassium is obtained, which is commonly called soft or granulated sulphate of potash. This soft sulphate is frequently dissolved in water or kelp liquor, and boiled till the solution stands about 50° Twaddle; when, on cooling, a crop of crystals is obtained of what is known as plate sulphate—a double sulphate of potassium and sodium, having essentially the composition $3K_2SO_4 + Na_2SO_4$. The following are Tatlock's analyses of samples of soft and plate sulphate obtained from kelp:—

Fig. 3.



	Soft Sulphate.	Plate Sulphate.
	Per Cent.	Per Cent.
Sulphate of potassium,	53·70	72·45
Sulphate of sodium	16·11	24·62
Chloride of potassium,	—	—
Chloride of sodium,	8·11	1·32
Carbonate of sodium,	2·77	—
Insoluble,	·87	1·05
Water,	18·72	·40
	100·28	99·84

The average production of sulphate of potash in the neighbourhood of Glasgow from kelp, during the last ten years, is estimated to be about 500 tons per annum.

Sulphate of potash is also obtained as a bye product in the manufacture of carbonate of potash, especially from beet-root molasses and ash of woollen sweat, from which sources about 2000 tons are produced annually. The following is an analysis by Clark of a sample of beet sulphate:—

	Per Cent.
Sulphate of potassium,	92·94
Chloride of potassium,	4·96
Carbonate of potassium,	·32
Carbonate of sodium,	·53
Insoluble,	.80
Water,	·35
	99·90

A peculiar compound of sulphate of potassium with sulphate and chloride of magnesium, called Kainit, is found in large quantity in the Anhalt Mine at Stassfurt and at Kalutz. When pure, according to Rammelsberg, it has the composition, $K_2SO_4,MgSO_4,MgCl_2 + 6H_2O$; but it is generally found mixed with chloride of sodium and chloride of potassium. The following are analyses of Stassfurt and Kalutz kainit:—

	Tatlock. Stassfurt.	Frank. Kalutz.	Clark. Stassfurt.
	Per Cent.	Per Cent.	Per Cent.
Sulphate of potassium,	16·98	20·30	25·32
Sulphate of magnesium,	—	14·20	14·19
Chloride of magnesium,	17·69	11·10	14·24
Chloride of sodium,	43·88	27·20	28·87
Chloride of potassium,	2·45	—	—
Sulphate of calcium,	2·72	2·80	2·72
Insoluble,	5·24	9·20	3·66
Water,	11·04	15·20	11·00
	100·00	100·00	100·00

Kainit is extensively employed and highly prized as a fertilizing agent, and it might be used for the manufacture of sulphate of potash; but hitherto its application as a manure has been found most advantageous. It is sometimes made artificially by mixing carnallit with kieserit and other salts.

Acid Sulphate of Potassium, $KHSO_4$. Synonyms, Bisulphate of Potash, *Sal-enixum;* German, *Zweifach schwefelsaures Kali;* French, *Bisulphate de Potasse.*

This salt is produced when nitric acid is made by the action of sulphuric acid on nitrate of potash, and it may be formed by heating 87 parts of the neutral sulphate with 49 parts of sulphuric acid. It is much more soluble in water than the neutral salt, and it has a strong acid reaction and taste. When heated

it melts about 197° C., and at a higher temperature (about 600° C.) it loses one-half of its sulphuric acid, partly in the form of sulphurous acid and oxygen. It is used principally for cleansing metals, separating silver from gold, and decomposing certain refractory minerals.

NITRATE OF POTASSIUM, KNO_3. Synonyms, Saltpetre, Nitre, Nitrate of Potash, and (in the fused state) Sal Prunelle; *Azotate de Potasse*, French; *Salpetersaures Kali* or *Kalisalpeter*, German.

Preparation.—1. By neutralizing solution of pure carbonate or hydrate of potassium with nitric acid, evaporating and crystallizing. 2. By mixing pure chloride or carbonate of potassium with pure nitrate of sodium, and crystallizing repeatedly.

Manufacture.—For commercial and manufacturing purposes this substance is obtained, either by washing natural or artificially prepared saltpetre earths with water, or by the mutual decomposition of chloride of potassium (muriate of potash) and nitrate of sodium (Chili saltpetre).

1. *By the Washing of Saltpetre Earths and Soils.*—When nitrogenous organic matter, either animal or vegetable, is exposed to atmospheric influences in presence of strong bases, nitrites and ultimately nitrates are formed by a process of oxidation known as "nitrification." Quite recently the action has been attributed to the presence of germs having the power of transferring oxygen. It is possible, but by no means certain, that ammonia is produced at an intermediate stage. This process goes on in nature on a vast scale, particularly in countries where vegetation abounds, and where the climate is warm and moist; but it must not be confounded with the formation of nitric acid by natural electrical discharges. In India, east of the Ganges, and particularly in the district of Tirrhût in Bengal, the saltpetre appears as a white efflorescence on and near the surface of the soils, which are gathered for its extraction—an operation which has been carried on in India from a very remote period. In recovering the saltpetre the earth is placed in wood boxes or "keaves," lixiviated with several successive waters, and the strong cold liquors thus obtained, which usually contain about 14 per cent. of nitrate of potassium, concentrated in iron pans and run into coolers to crystallize. A crop of very impure crystals is thus obtained, which contains, besides sulphate and chloride of potassium, a large amount of common salt. These are treated with a limited quantity of boiling water, just sufficient to dissolve the nitrate of potassium, and leave a large proportion of the other salts behind. The hot liquors, on cooling, deposit another crop of nitre, which is the article known in the British market as "Indian" or "Bengal" saltpetre. OTTO gives the following example of the results obtained in the lixiviation of the earth:—32 cubic feet of earth containing 80 lbs. saltpetre, treated with 1000 lbs. water, gave 500 lbs. solution containing 40 lbs. saltpetre; and the residue treated with 500 lbs. water, gave 500 lbs. solution containing 20 lbs. saltpetre, and so on—each succeeding 500 lbs. of water giving the same quantity of liquor containing half the previous amount. The following table (XXV.) gives analyses by TATLOCK of this product, which fairly represent it as usually imported into this country:—

TABLE XXV.

	Bengal Ordinary Commercial.		Bombay Crude.	
	1.	2.	3.	4.
Nitrate of potassium,....	96·51	89·36	72·46	36·06
Sulphate of potassium,...	·89	·75	·13	2·64
Chloride of potassium,....	·84	4·57	6·65	—
Nitrate of sodium, ...	—	—	—	·26
Chloride of sodium,.....	·20	·31	17·41	47·43
Sulphate of calcium, ...	—	—	·19	2·21
Nitrate of magnesium,....	—	1·97	·17	2·08
Insoluble,.....	·21	·14	·14	1·55
Water,.....	1·35	2·90	2·85	7·95
	00·00	100·00	100·00	100·18

It will thus be seen that in East Indian saltpetre, as imported, there are present both sulphate and chloride of potassium, although this fact is not usually recognized in the commercial analysis or "refraction" of saltpetre generally given, and which does not involve an estimation of the potassium. The refining of this product for the various purposes to which it is applied is carried out, in this country, in the same way as the purification of artificial saltpetre by the process hereafter described. In some districts where potassium is not plentiful in the soil, nitrates of sodium, calcium, and magnesium partially replace the nitrate of potassium; and in that case it is necessary to add some carbonate of potassium—usually obtained from wood ashes—to the first liquors, in order to convert all these into the potassium nitrate, the calcium and magnesium being thrown down as carbonates, insoluble in the liquor. A sample of the residual salts left on the treatment of the first crop of crude saltpetre with hot water, known as "East Indian refuse," was found to contain—

	Per Cent.
Sulphate of potassium,.....	8·83
Nitrate of potassium, ...	13·15
Chloride of potassium, ...	21·14

About 12,500 tons of saltpetre from this source were imported into Great Britain in 1876.

In several countries on the continent of Europe saltpetre was formerly made in large quantity, artificially, in imitation of the natural process, by mixing all kinds of refuse animal matters with old plaster rubbish, ashes, and any kind of basic material of a porous nature, forming what are called "saltpetre beds," which were exposed to the influence of air and moisture for some months, then taken down and the material lixiviated; the liquors which contained the nitrate, chiefly as the calcium salt, being then treated with carbonate of potassium, obtained either from the ashes of wood or beet-root. In France, during the Peninsular War, about 2000 tons a year were made in this way; and in that country, as well as in Sweden and other parts of Europe, the manufacture is still carried on to a very limited extent for local consumption. In Switzerland the flooring of stables and cow houses is

sometimes made with a kind of marl, with the object, by the addition of wood ashes, of recovering saltpetre from the nitrate of calcium.

2. *From "Nitrate of Soda" and "Muriate of Potash."*—This process was originally devised by LONGCHAMP, ANTHON, and KUHLMANN, and is the one by which the greater proportion of the saltpetre used in this country is procured. The chloride of potassium does not require to be of very high strength, nor particularly free from chloride of sodium, as the latter salt is formed in large quantity as a bye product of the decomposition; but it is most economical to employ it of about 90 per cent., which generally contains from 5 to 8 per cent. of chloride of sodium. The nitrate of sodium used shows most commonly a strength of about 95 per cent.; but although it is not necessary to work with any special quality of either of these two raw materials, it is always advisable to determine by analysis the composition of both to begin with, so that the two may be added to each other in such proportions that one equivalent of pure chloride of potassium shall act upon one of pure nitrate of sodium, according to the following equation:—

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Theoretically, therefore, 74·6 parts of pure chloride will require 85 of pure nitrate, producing 101·1 of pure saltpetre and 58·5 of common salt. The process, when properly conducted, yields, on the one hand, practically pure saltpetre, and, on the other, chloride of sodium almost quite free from any potassium salt; so that there is very little loss of material except what is incurred in a mechanical way, and which is unavoidable. The commercial nitrate of sodium always contains a small quantity of sulphate, and sometimes even nitrate of potassium, which are derived from the "caliche" or "terra salitrosa," from which it is made; and as the sulphate is available for the formation of saltpetre, it should be allowed for in weighing out the materials. The following table (XXVI.) of analyses of the crude and commercial nitrate shows the proportions of potassium salts in each:—

TABLE XXVI.

	Caliche.		Commercial Nitrate of Soda, Good Quality.	
	1.	2.	3.	4.
Nitrate of sodium,	62·61	47·829	97·448	95·24
Nitrate of potassium,	6·67	—	—	2·83
Sulphate of potassium,	2·09	4·64	·07	—
Chloride of sodium,	24·54	27·97	·30	·39
Sulphate of sodium,	—	—	·07	—
Iodate of sodium,	·10	·28	·022	trace.
Iodide of sodium	absent.	·011	—	—
Sulphate of calcium,	·34	2·16	trace.	trace.
Nitrate of magnesium,	trace.	1·29	·25	trace.
Insoluble: Silica,		10·43		
Insoluble: Alumina,	3·24	1·00	·18	·04
Insoluble: Oxide of iron,		·39		
Insoluble: Lime,		·25		
Water,	·41	3·75	1·66	1·50
	100·00	100·00	100·000	100·00
Analyst,	TATLOCK.	CLARK.	TATLOCK.	CLARK.

The proper quantities, as based on the analyses, having been weighed out, the "muriate" is dissolved in boiling water, the solution having a specific gravity of about 1·2, and the "nitrate of soda" then added in the solid form. The decomposition commences at once, and chloride of sodium begins to "drop;" one-fourth of the liquor is then evaporated off, during which salt constantly falls, and is fished out, and placed upon iron drainers fixed over the pots. The fires are now drawn, the solution settled for an hour or two to clear, and run into coolers, in which the crystallization takes place, a first crop of large and impure crystals being obtained, which contain from 2 to 10 per cent. of chlorides. The mother lyes are run off, and the crude saltpetre roughly refined, by dissolving in boiling water to a specific gravity of about 1·5, cooling, and crystallizing. The product is now much purer, but not sufficiently so for such purposes as the manufacture of gunpowder, for which it must be further refined by the method described hereafter. The common salt, after being drained, is transferred to washing boxes, and washed by repeated digestions with boiling water, till the last washings have a density of only 1·205, showing that the saltpetre has all been washed out, and that common salt alone is being dissolved. In the following table (XXVII.) are analyses of the washed salt thus obtained:—

TABLE XXVII.

	1.	2.	3.	4.
Chloride of sodium,	95·50	94·88	91·52	88·08
Nitrate of potassium,	·21	·20	·18	·24
Sulphate of potassium,	·17	trace	·11	1·92
Sulphate of sodium,	—	—	—	·86
Carbonate of sodium,	—	—	—	1·00
Sulphate of calcium,	·09	—	—	—
Chloride of magnesium,	·07	—	—	—
Insoluble,	1·65	·62	·87	1·05
Water,	2·35	4·30	7·25	6·85
	100·04	100·00	99·90	100 00
Analyst,	CLARK.	TATLOCK.		

The analysis of No. 4 salt given above shows that the process of manufacture has been conducted imperfectly, nearly 2 per cent. of sulphate of potassium being lost in the salt, which might otherwise have been recovered in the form of nitrate. This salt is used for agricultural purposes, and also for roasting cupreous pyrites cinders in the extraction of copper by the wet method.

The washings and the mother liquors are concentrated, and used in place of water to dissolve the raw materials in the next charge. In course of time they become impure from the accumulation of thiosulphates, and salts of iodine derived from the nitrate of sodium, and even from the kelp muriate of potash, if the latter be employed. Bromide of sodium is also present in considerable quantity in the old liquors, from the German muriate of potash, which is the variety most commonly used. Both iodine and bromine may be recovered from these liquors. The following is a complete analysis, by

Tatlock, of mother liquor from crude saltpetre, in the manufacture of which muriate of potash from kelp was principally used; but the proportions of the principal salts must necessarily vary according to temperature:—

	Per Cent.	
Nitrate of potassium,	15·18	
Chloride of potassium,	1·00	
Sulphate of sodium,	2·77	
Chloride of sodium,	19·45	
Thiosulphate of sodium,	2·14	
Iodide of sodium,	1·00	= 826 grains iodine per gal.
Bromide of sodium,	—	
Water,	58·46	
	100·00	
Specific gravity,	1·394	

Clark found in two other samples of old mother liquor, in the production of which German muriate had been chiefly used—

	Grains per Gallon.	
	1.	2.
Iodine as iodide,	140·00	33·44
Iodine as iodate,	5·30	2·67
Total iodine,	145·30	36·11
Bromine as bromide,	1365·00	—
Bromine as bromate,	729·50	—
Total bromine,	2094·50	—

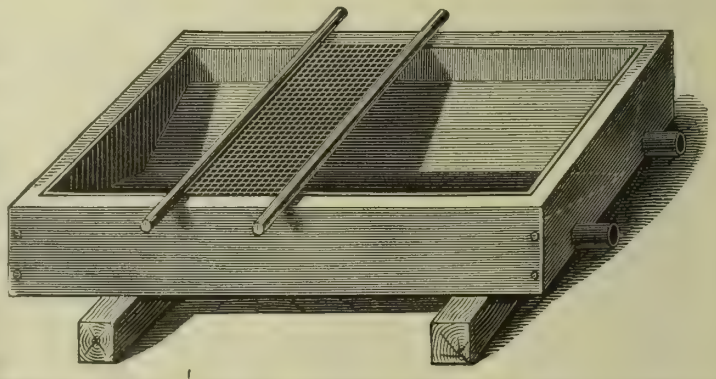
If "German muriate" is employed it is desirable to add as much soda ash, after it is dissolved, as will precipitate the small quantity of chloride of magnesium which it contains; as otherwise traces of the last-named substance are very apt to remain in the nitre after it is refined, whereby the latter has a tendency to deliquesce—an effect which would also be produced by any excess of nitrate of sodium. The "muriate of potash" obtained from kelp is free from chloride of magnesium, and therefore with it no such precaution is required; but it contains from 4 to 6 per cent. of sulphate of potassium, which has been objected to on the ground that it does not decompose completely with nitrate of sodium; but this is erroneous, as when a large excess of chloride of sodium is present, as is always the case in the process, the action is almost perfect, and the washed salt shows only about ¼ per cent. of sulphate of potassium. Some manufacturers even decompose the sulphate by addition of chloride of barium, by which chloride of potassium is formed, and sulphate of barium thrown down. The pots, which are hemispherical with vertical sides, are set on a pillar of brick-work, and are boiled by direct heat, the flue passing round the entire curve of the pot; and they are of sufficient capacity to hold about 2 tons of saltpetre in hot saturated solution.

A greatly improved mode of operating has been introduced, however, which has been in use in a Scotch saltpetre manufactory for many years. According to this method the double decomposition of the chloride of potassium and nitrate of sodium is effected in a cylindrical iron pan, the boiling being accomplished by a steam coil served with steam of 60 lbs. pressure, and the vapours being drawn off by a pipe connected with the chimney-stalk. A stirring apparatus, fixed to a vertical shaft driven by machinery, keeps the precipitated common salt from settling. The liquor having been concentrated to some extent, the whole contents are discharged into coolers, through a strainer which retains the salt and insoluble matters. The saltpetre liquor is quickly cooled by a constant stream of water which flows round the vessel externally, and it is at the same time stirred by machinery. The crystals are thus obtained very small and fine, which enables them to be easily washed afterwards with cold water. Saltpetre thus prepared is said to contain not more than ·1 per cent. of chlorides, and does not require refining except for some special purpose, such as the manufacture of sporting gunpowder. Fig. 1, Plate I., under article Iodine, is a sketch of the evaporating pan.

In Germany, the "schlempekohle" or crude carbonate of potassium, obtained from beet-root molasses, was until recently largely employed in place of "muriate of potash" in the manufacture of saltpetre—a process which was introduced by M. Wöllner; but now the cheapness and abundance of the muriate from the Stassfürt deposits is such that it is most commonly used.

Refining of Saltpetre.—What is known as the French process is the one commonly employed, whether the crude material is native "Indian" or "Artificial." It consists in dissolving the rough saltpetre in boiling water, or rather making a hot saturated solution, which should show a density of about 1·5, boiling for a short time with a little dissolved glue, which coagulates, entangling insoluble matters and carrying them to the bottom, but partly to the surface of the liquor; which after being settled is run into shallow pans surrounded by cold running water, and agitated during the rapid cool-

Fig. 4.



ing, either by means of wood rakes or by stirring gear driven by machinery. The saltpetre "flour" is fished out of the liquor by flat perforated shovels, and thrown upon a wire-gauze strainer placed over the cooler. Fig. 4 is a sketch of the cooler and strainer used.

It is then thrown into a box and washed by several successive steeps with cold water, by which the mother liquor containing the chlorides is washed away and the saltpetre left almost chemically pure. The whole process of refining, as well as that of washing the salt, is based upon the fact that saltpetre is immensely more soluble in hot water than in cold, while the chloride of sodium is nearly equally so in both, so that the hot saturated solution of the former deposits but little of the latter on the liquor being cooled; and also from the slight solubility of the saltpetre in cold water but little is dissolved in the final washing. The following is an analysis, by TATLOCK, of the mother liquor from refined saltpetre:—

	Per Cent.
Nitrate of potassium,.....	14·60
Chloride of potassium,.....	2·00
Sulphate of sodium,.....	1·63
Chloride of sodium,.....	7·85
Thiosulphate of sodium,.....	·64
Water,.....	73·28
	100·00
Specific gravity,.....	1·220

In Great Britain and Ireland not less than 17,000 tons of artificial saltpetre are made, besides many thousand tons in Germany and France, some of which, as imported into this country, is remarkably pure, containing less than ·005 per cent. of chlorides. At the present time (1878) about 2000 tons per annum are imported from Germany alone.

It is commonly supposed that sulphate of potassium will not produce the nitrate by double decomposition with nitrate of sodium, and that is quite the case if only equivalent quantities of the two salts are employed; but it was observed by Mr. WILLIAM HENDERSON, of Glasgow, in 1861, that by using 2 equivalents of nitrate of sodium the reaction was complete, and he not only shortly thereafter made some tons of pure nitrate of potassium in this way for the market, but purified the residual sulphate of sodium (Glauber's salt), which was sold for calico-printers' use. At that time "muriate of potash" was worth upwards of £20 per ton, and sulphate being much less expensive, there was some inducement to use this process; but there is none now, the muriate being little over a third of the price which it brought then. Equivalent proportions of nitrate of sodium and sulphate of potassium are likewise mutually decomposed with production of nitrate of potassium, when a large excess of chloride of sodium is present.

It was proposed by ROWLANDSON, more than twenty years ago, to use the liquors direct from kelp for the preparation of saltpetre, a process which has since been described by THEROULD. This has been done in France, but in this country the method has not been tried except on an experimental scale. The following table (XXVIII.) gives analyses, made by TATLOCK, of the rough, intermediate, and refined artificial saltpetre:—

TABLE XXVIII.

	Rough.	Intermediate.	Refined.		
	1.	2.	3.	4.	5.
Nitrate of potassium,.	80·36	99·22	99·663	97.54	97·02
Sulphate of sodium,..	2·43	trace	—	—	—
Chloride of sodium,..	11·07	·41	·007	·03	·08
Sulphate of calcium,..	—	—	—	trace	—
Nitrate of magnesium,	—	—	—	.28	—
Insoluble,.....	0·4	·02	—	·05	—
Water,.....	6·10	·35	·330	2·10	·290
	100 00	100·00	100·000	100·00	100·00

It has been proposed to obtain saltpetre by the action of nitrate of barium on sulphate of potassium, by which sulphate of barium (*blanc fixe*) is precipitated, and nitrate of potassium left in solution. The nitrate of barium is procured by the double decomposition of nitrate of sodium with chloride of barium, the latter being produced by exposing native carbonate of barium (*witherite*) to the fumes of hydrochloric acid. According to WAGNER this process should be remunerative, and at first sight it would seem to be so, the precipitated sulphate of barium being a marketable article of some value; but a scrutiny of the process renders it difficult to understand how there can be any advantage in it, the last-named product not being worth much more than would cover the extra cost of sulphate of potassium over that of the chloride; and working on a large scale with precipitates, which require much washing, is necessarily tedious and expensive.

The employment of carbonate of potassium for producing saltpetre with nitrate of sodium, introduced into Germany by WOLLNER in 1854, is now rapidly giving place to that of chloride of potassium, obtained from carnallit and other sources.

A few years ago there was introduced into this country from South America a crude saltpetre, which consisted chiefly of nitrate of sodium with much smaller and variable quantities of nitrate of potassium. The following table (XXIX.), shows the composition of several samples of this product:—

TABLE XXIX.

	1.	2.	3.	4.	5.
Nitrate of potassium,	25·90	23·18	18·20	16·48	16·22
Sulphate of potassium	·52	3·24	·37	·43	·65
Nitrate of sodium,...	68·882	51·642	76·385	77·084	77·39
Chloride of sodium,..	1·50	16·27	2·23	2·80	2·96
Iodate of sodium,....	·062	·238	·055	·066	trace.
Iodide of sodium,....	·036	—	—	—	—
Sulphate of calcium,	trace.	·19	·12	·12	·12
Nitrate of magnesium,	·60	1·52	·35	·42	·47
Insoluble,.....	·05	·12	·04	·05	·04
Water, ...	2·45	3·60	2·25	2·55	2·15
	100·000	100·000	100·000	100·000	100·00
Analyst,.....	CLARK.	TATLOCK.			

This mixed salt is evidently made by simply concentrating the mother liquors from the caliche until the crop of crystals obtained by cooling contains a

sufficient proportion of saltpetre. It is quite plain that the nitrate of potassium in this article could never realize the market value of saltpetre, as the entire product would in any case require to be dissolved; and when in solution it would not be worth more than the whole nitrate taken as nitrate of sodium, plus the potassium reckoned as chloride.

Applications.—Of the 32,000 tons of commercial nitrate of potassium made in and imported into this country, nearly 30,000 tons are consumed in the manufacture of gunpowder and other explosives, and much is also used in the curing of meat.

In medicine it is used as an irritant, sedative, and diuretic.

Properties.—Pure nitrate of potassium crystallizes in large anhydrous hexagonal prisms with dihedral termini. It has a cooling and saline taste, and is neither hygroscopic nor deliquescent. Heated to 340° C. it fuses to a transparent liquid, and decomposes slightly with liberation of a small quantity of oxygen, which is retained by the fluid and evolved at the moment of solidification. The specific gravity of nitrate of potassium (fused) is 2·06 (PAGE and KEIGHTLEY). At a red heat it loses a very appreciable quantity of oxygen, and is, in consequence, partially reduced to nitrite (KNO_2), and at a still higher temperature oxides of potassium are formed. When fused with carbon and sulphur violent combustion ensues; these substances are oxidised to the greatest posible limit, carbonate and sulphate of potassium being produced; and many ordinary combustibles treated similarly burn with explosive violence. It is highly soluble in boiling water, 100 parts at 100° C. taking up about 240 parts of it; but it is rather insoluble in cold water, 100 parts dissolving only 26 parts at 15·°6 C., forming a solution which contains 21 parts in 100.

The following table (XXX.), by SCHIFF, shows the proportions of nitrate of potassium corresponding to various densities, at 16° C.:—

TABLE XXX.

Specific Gravity.	KNO_3, Per Cent.	Specific Gravity.	KNO_3, Per Cent.
1·0058	1	1·0819	13
1·0118	2	1·0887	14
1·0178	3	1·0956	15
1·0239	4	1·1026	16
1·0300	5	1·1097	17
1·0363	6	1·1169	18
1·0425	7	1·1242	19
1·0490	8	1·1316	20
1·0555	9	1·1390	21
1·0621	10	1·1464	22
1·0686	11	1·1538	23
1·0752	12	1·1613	24

The subjoined table (XXXI.), by GAY-LUSSAC, gives its solubility at different temperatures:—

TABLE XXXI.

Temperature.	KNO_3 dissolved by 100 of Water.	Temperature.	KNO_3 dissolved by 100 of Water.
Degrees C.		Degrees C.	
0·	13·32	45·10	74·66
5·01	16·72	54·72	97·05
11·67	22·23	65·45	125·42
17·91	29·31	79·72	169·27
24·94	38·40	97·66	236·45
35·13	54·82		

The following extract from the *Journal of the Chemical Society*, vol. xxv. page 567, includes excellent tables, based upon carefully conducted experiments by PAGE and KEIGHTLEY, of the solubilities of nitrate of potassium and the other salts which appear in its preparation, and which will be found most useful by manufacturers:—

Chloride of Sodium.

Specific gravities of solutions by digestion at—

15°·6 C.	100° C. Cooled down to 15°·6 C.
1204·19	1211·48
1204·03	1206·93

100 parts of water dissolve—

35·76	36·26

Contained in 100 parts of solution—

26·34	26·61

Chloride of Potassium.

Specific gravities of solutions by digestion at—

15°·6 C.	100° C. Cooled down to 15°·6 C.
1171·72	1171·94
1171·45	1171·71

100 parts of water dissolve—

32·88	32·06

Contained in 100 parts of solution—

24·74	24·84

Nitrate of Sodium.

Specific gravities of solutions by digestion at—

15°·6 C.	100° C. Cooled down to 15°·6 C.
1378·15	1378·43
1378·32	1378·17

100 parts of water dissolve—

84·21	84·69

Contained in 100 parts of solution—

45·71	45·85

Nitrate of Potassium.

Specific gravities of solutions by digestion at—

15°·6 C.	100° C. Cooled down to 15°·6 C.
1141·68	1142·25
1141·23	1141·32

100 parts of water dissolve—

26·04	26·30

Contained in 100 parts of solution—

20·66	20·82

Sulphate of Potassium.

Specific gravity of solution by digestion at 15°·6C.,	1176·84
100 parts of water dissolve,	9·26
100 parts of solution contain,	8·48

The following tables will afford a comparative view of these results. The solubility of one part of salt, deduced from the above experiments, is also shown, and the value of the specific gravities in degrees of TWADDELL'S hydrometer is attached for technical purposes.

I. Table showing the specific gravities and degree of solubility by digestion of the salts, at a constantly maintained temperature of 15°·6 C. = 60°·08 Fahr.:—

	Specific Gravity.	Degrees Twaddell.	Contained in 100 Parts Saturated Solution.	100 Parts of Water Dissolve	1 Part of Salt Soluble in Parts of Water.
NaCl,.....	1204·03	40·8	26·34	35·76	2·79
KCl,.....	1171·58	34·2	24·74	32·88	3·04
$NaNO_3$,....	1378·32	75·6	45·71	84·21	1·18
KNO_3,.....	1141·23	28·2	20·66	26·04	3·84
K_2SO_4,.....	1176·84	35·4	8·48	9·26	10·79

II. Table showing the specific gravities and degree of solubility by saturation at 100° C., and subsequent cooling down to 15°·6 C. = 60°·08 Fahr.:—

	Specific Gravity.	Degrees Twaddell.	Contained in 100 Parts Saturated Solution.	100 Parts of Water Dissolve	1 Part of Salt Soluble in Parts of Water.
NaCl,.....	1206·93	41·4	26·61	36·26	2·75
KCl,.....	1171·82	34·4	24·84	33·06	3·02
$NaNO_3$,....	1378·43	75·7	45·85	84·69	1·18
KNO_3,.....	1142·25	28·5	20·82	26·30	3·80

Estimation of the specific gravities of the nitrates and chlorides of sodium and potassium. The nitrates were rendered anhydrous by careful fusion, and the chlorides by ignition. Specific gravities at 15°·6 C.:—

	In Absolute Alcohol.	In Pure Oil of Turpentine
KNO_3,.....	2·06	2·06
$NaNO_3$,.....	2·24	2·25
KCl,.....	1·90	1·91
NaCl,.....	2·08	2·06

Similar results were attained in another series of estimations, where the salts had been dried over oil of vitriol.

In the last set of experiments the specific gravities and degrees of solubility of these salts, in presence of each other, were determined; and the results show that, although a solution already saturated by a given salt is still capable of taking up other salts, the degrees of solubility of all present in solution are considerably lessened. In the analysis of the mixed salts the potassium, chlorine, and nitric acid were determined directly.

I. Solution saturated with chloride of sodium and chloride of potassium at 15°·6 C. Specific gravity, 1233·74 (= 46°·75 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
KCl,.....	13·92	9·62
NaCl,.....	30·65	21·21

II. Solution saturated with nitrate of sodium and nitrate of potassium at 15° 6 C. Specific gravity, 1478·22 (95°·64 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
KNO_3,.....	34·53	15·29
$NaNO_3$,.....	91·16	40·39

III. Solution saturated with nitrate of potassium and chloride of sodium at 15°·6 C. Specific gravity, 1330·92 (66°·18 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
KNO_3,.....	32·32	18·79
NaCl,.....	39·57	23·03

IV. Solution saturated with chloride of sodium, chloride of potassium, and nitrate of potassium, at 15°·6 C. Specific gravity, 1329·74 (65°·95 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
KCl,.....	1·39	·82
NaCl,.....	38·58	22·51
KNO_3,.....	31·44	18·33

V. Solution saturated with nitrate of potassium, nitrate of sodium, and chloride of sodium, at 15°·6 C. Specific gravity, 1438·63 (87°·72 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
NaCl,.....	26·44	12·65
$NaNO_3$,.....	53·68	25·68
KNO_3,.....	28·92	13·83

VI. Solution saturated with sulphate of potassium and chloride of sodium at 15°·6 C. Specific gravity, 1241·51 (48°·30 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
K_2SO_4,.....	7·19	4·99
NaCl,.....	36·71	25·52

VII. Solution saturated with sulphate of potassium, chloride of potassium, and chloride of sodium, at 15°·6 C. Specific gravity, 1250·42 (50°·1 Twaddell):—

	100 Parts of Water Dissolve	100 Parts of Saturated Solution Contain
K_2SO_4,.....	4·69	3·19
KCl,.....	10·11	6·88
NaCl,.....	32·15	21·88

POTASSIUM CHLORATE, $KClO_3$. Synonyms, Chlorate of Potash; *Chlorate de Potasse*, French; *Chlorsaures Kali*, German.

Preparation.—1. By passing chlorine in excess through solution of hydrate or carbonate of potassium, and repeatedly crystallizing. The following action takes place:—

$$6KHO + 3Cl_2 = 5KCl + 3H_2O + KClO_3.$$

2. By heating chlorate of calcium with chloride of potassium, both in solution, thus:—

$$Ca2ClO_3 + 2KCl = CaCl_2 + 2KClO_3.$$

Carbonate or sulphate of potassium may be substituted for the chloride.

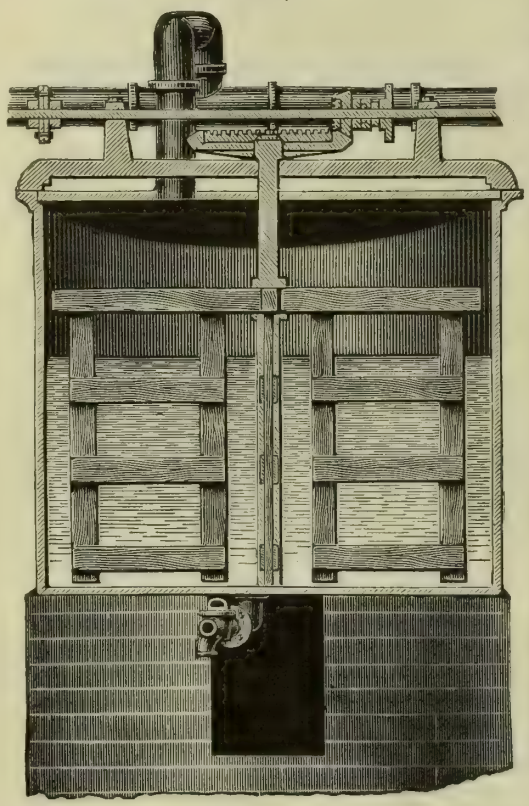
3. By passing chlorine gas in excess through cream of lime and chloride of potassium, with the aid of heat, thus:—

$$3CaH_2O_2 + KCl + 3Cl_2 = 3CaCl_2 + 3H_2O + KClO_3.$$

Manufacture.—All these processes have been employed in the preparation of chlorate of potassium on the commercial scale, but it is the last-named one, devised by GRAHAM, which is now universally adopted. The chlorine is generated in large octagonal vessels, each side of which consists of a slab of "Derbyshire flagstone," the bottom being constructed of two large and heavy blocks. The edges are grooved for the insertion of india-rubber ropes, which, when the iron girders surrounding the vessel are tightly compressed by screw-bolts, make an excellent joint. The gas is conducted by stoneware pipes into the mixture, which is contained in covered iron cylinders, fitted with iron stirring

apparatus driven by steam power. The annexed sketch (Fig. 5), shows the stirrer employed. No external heat is required, as the action is sufficiently strong to elevate the temperature to the requisite degree. At first only hypochlorite of calcium is produced, but at a further stage the chlorate of potassium is formed, and remains in solution along with the chloride of calcium. The liquors are crystallized in iron coolers, when the first crystals of crude chlorate separate of a slightly brown colour, leaving the chloride of calcium in solution. These are dissolved in lead or lead-lined vessels, by the smallest quantity of boiling water, the temperature being maintained, during the solution, by steam, and recrystallized, producing a crop which is almost chemically pure.

Fig. 5.

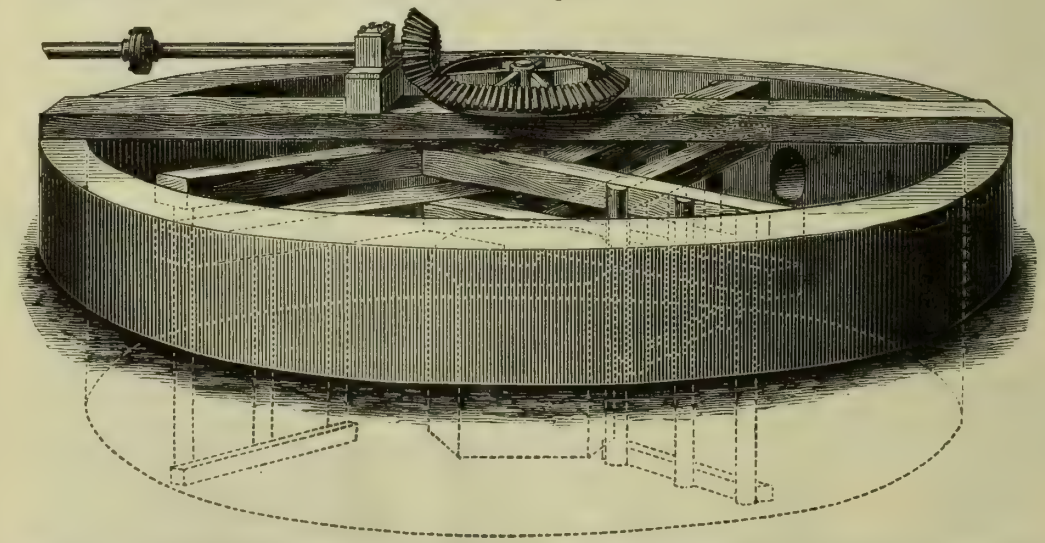


The recovery of the manganese from the waste liquors is an important point in connection with this manufacture. At the works of the North British Chemical Co., near Glasgow, where the chlorate is made on a large scale, the spent liquors are run into a tankbuilt of concrete, and fitted with stirring gear, of which the following (Fig. 6) is a sketch. The liquors are there neutralized, and excess of lime added during agitation; then pumped into the tower, where air is blown through the mixture by a blowing engine, to oxidise the monoxide to the higher oxide of manganese. The process of recovery, when thus carried out on a first-rate scale, involves a complete Weldon plant. The following table (XXXII.) gives analyses by TATLOCK of two samples of commercial chlorate of potassium:—

TABLE XXXII.

	1.	2.
Chlorate of potassium,	99·75	99·59
Sulphate of potassium,	—	trace.
Chloride of potassium,	·05	·07
Insoluble,	—	·10
Water,	·20	·30
	100·00	100·06

Fig. 6.



There are probably about 2000 tons of this salt made annually in the United Kingdom at the present time, and about half as much on the continent of Europe.

Applications. — Chlorate of potassium is largely used in dyeing and calico printing as an oxidiser, and chiefly for the preparation of aniline-black. A great quantity is consumed in the manufacture of lucifer matches and of fireworks, and it is used to mix with fulminate of mercury in the production of detonators for exploding dynamite. It is from this substance also that oxygen gas is most commonly made, and it is employed medicinally in fevers and cancers.

Properties.—Chlorate of potassium crystallizes in the form of rhomboidal tables, which have a saline and cooling taste. Heated to a temperature approaching redness it fuses and decomposes, evolving the whole of its oxygen if the heat be sufficiently high, and leaving only chloride of potassium as a residue. Heated with any combustible matter it parts with its oxygen with great rapidity, causing violent deflagration. It is rather insoluble in cold, but dissolves with great facility in boiling water. The following table (XXXIII.), constructed by GAY-LUSSAC, represents the solubility of chlorate of potassium at different temperatures:—

TABLE XXXIII.

Temperature.	Parts $KClO_3$ Dissolved by 100 Parts Water.	Temperature.	Parts $KClO_3$ Dissolved by 100 Parts Water.
Degrees C.		Degrees C.	
0·	3·33	35·02	12·05
13·32	5·60	49·08	18·96
15·37	6·03	74·89	35·40
24·43	8·44	104·78	60·24

Its solubility in solution of chloride of calcium is considerably less than in water.

POTASSIUM SILICATE, $K_2O,4SiO_2$. Synonyms, Tetrasilicate of Potash, Soluble Potash Glass; *Silicate de Potasse*, French; *Kieselsaures Kali*, German.

Preparation.—1. By boiling pure precipitated silica with caustic potash solution. 2. By fusing pure silica with pure carbonate of potassium.

Manufacture.—This substance is prepared by fluxing together white sand (silica), carbonate of potassium, and a little charcoal in a reverberatory furnace, till intumescence ceases, showing that all the carbonic anhydride has been displaced. The result is a transparent glass with a strong tinge of blue or green, resembling that of glacier-ice, due to the presence of iron. The proportions of the ingredients employed are approximately—

White sand,	45 parts.
Carbonate of potassium,	30 "
Wood charcoal (powder),	3 "
	78 "

The product is 58 parts of silicate. The object of the charcoal is to assist in the expulsion of carbonic anhydride by reducing it to carbonic oxide. Frequently the potash is largely replaced by soda, even to the extent of one half. It is desirable to have the carbonate as free as possible from sulphates, in order to avoid the formation of sulphides. It is sold both in the solid condition and in the state of thick solution, which is obtained by heating the solid in powder in close digesters by superheated steam; but prolonged boiling also dissolves it. The "liquid silicate" thus obtained is a thick transparent fluid, which may have as high a specific gravity as 1·35. It is at this stage that the soda is usually introduced, in the form of silicate solution, although it is sometimes added as soda ash in the fluxing process. Occasionally a small quantity of saltpetre is employed to assist in the melting. A mixed silicate of potassium and sodium may be obtained by using, instead of the ordinary carbonate of potassium, the carbonaceous mixture obtained by calcining Rochelle salt (tartrate of potassium and sodium) in close vessels. It has been proposed to prepare silicate of potassium by heating flints to redness, throwing them into water to disintegrate them, grinding, and boiling the powder with solution of caustic potash. This method does not seem to have been adopted, however, to any extent. In the following table (XXXIV.) are given analyses, by TATLOCK, of some samples of commercial silicate of potassium, both solid and liquid:—

TABLE XXXIV.

	1.	2.	3.		4.		5.	
	Solid.	Solid.	Liquid.	Solids from Liquid.	Liquid.	Solids from Liquid.	Liquid.	Solids from Liquid.
Potash (as silicate),	23·54	22·91	9 46	26·76	4·31	12·64	3·49	12 96
Soda (as silicate),	1·28	1·28	1·52	4·30	4·20	12·32	1·80	6·68
Silica,	65·60	66·84	23·28	65·88	24·32	71·28	16·64	61·81
Sulphate of potassium,	·87	1·08	·67	1·90	·61	1·79	1·48	5·48
Chloride of potassium,	·48	·48	·41	1·16	·67	1·97	3·52	13·07
Alumina and oxide of iron,	·40	·32	—	—	—	—	—	—
Water,	7·83	7·09	64·66	—	65·89	—	73·07	—
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Specific gravity.,	..	—	1·351	—	—	—	1·235	—

The total quantity of silicate of potassium made in the United Kingdom is very small, probably not exceeding 20 tons per annum.

Applications.—The greater part of the silicate of potassium made in this country is employed for mixing with potash and soda soaps—a purpose to which silicate of sodium is also largely applied.

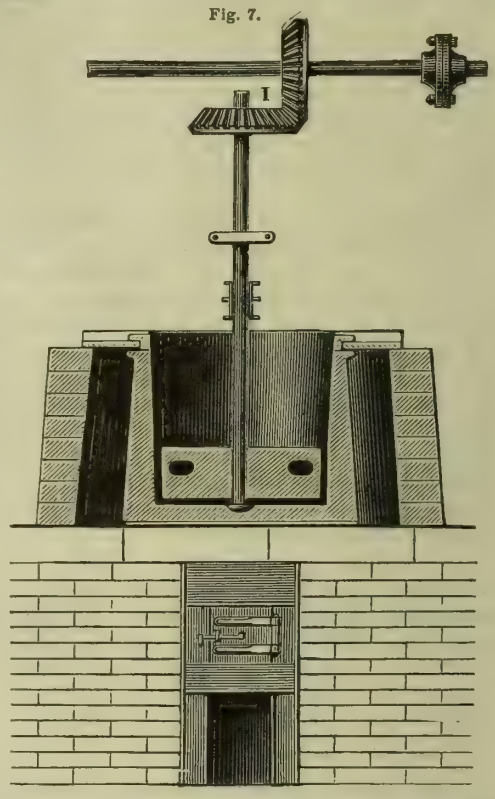
Properties.—Silicate of potassium is a transparent glass, soluble with difficulty in water. Its solubility as compared with insoluble potash glass is due to its

containing more potassium. FARADAY and BENRATH found two samples of common insoluble potash glass to contain respectively 11·61 and 13·67 per cent. of potash (K_2O), which, as will be seen by comparison with the analyses given above, is less than that contained in the soluble silicate of potassium. Its solution, which is alkaline, has detergent properties, and is decomposed by all strong acids, with liberation of gelatinous silicic acid. Fabrics impregnated with this substance, or with the corresponding sodium compound, are rendered incombustible.

POTASSIUM FERROCYANIDE ($K_4FeC_6N_6$, anhydrous; $K_4FeC_6N_6 + 3H_2O$, crystals).—Synonyms, Yellow prussiate of potash, Ferro-prussiate of potash; *Prussiate jaune de potasse*, French; *Ferrocyankalium* or *Blutlaugensalz*, German. This salt was first obtained, upwards of a century ago, by MACQUER, who prepared it by the action of a solution of potash on Prussian blue. It was first manufactured on the large scale at Campsie, near Glasgow, in 1807–8, and was introduced into calico-printing by CHARLES MACINTOSH of that place.

Manufacture.—It is now produced on a comparatively large scale, and in a state of great purity, by the mutual action, at a strong red heat, of nitrogenous animal matter, carbonate of potassium, and metallic iron—the materials and method used not differing greatly from those originally employed. The process may be said to consist of three stages—1st, the preparation of the "cake" or "metal," which is the mass resulting from the action of the ingredients at a high temperature; 2nd, the lixiviation of the cake; and 3rd, the crystallizations. The usual mode of operating is as follows:—The best carbonate of potassium, containing not more than 3 per cent. of carbonate of sodium, is placed in charges of about 80 lbs. each in small heavy cast-iron pots of about 18 inches diameter. These, which are 3 or 4 inches thick, are built vertically in a row over suitable furnaces, each being provided with a stirrer, consisting of a pair of perforated iron blades fixed to the bottom of a vertical shaft, a series of the latter being wrought by a horizontal one driven by steam power. The pots having been previously heated, the charges are introduced and brought up to an intense red heat, which insures the perfect fusion of the contents. At this stage the animal matter is introduced through an opening, which closes with a sliding lid in the iron cover, in small quantities at a time, in order to obtain the most perfect possible admixture of the materials, which are regularly stirred during the operation. The organic matter is at once decomposed, part of its nitrogen combining with carbon to form cyanogen (CN), while a further portion of the carbon reduces the alkaline carbonate to potassium, which at once combines with the cyanogen in the nascent state, producing cyanide of potassium (KCN). Sometimes iron is introduced in the form of turnings or borings; but this does not seem to be essential, as in any case the metal of the pots is disintegrated and yields a sufficient supply. The following (Fig 7) is a sketch of the pot and stirring apparatus used:—

Fig. 7.



The animal matters employed are chiefly those given in the table beneath, in which also the proportion of nitrogen usually present in each is stated:—

	Per Cent.
Horns and hoofs,	14 to 16
Dried blood,	14 to 16
Wool and hair clippings,	10 to 16
Feathers,	15 to 17
Leather parings,	6 to 8

To a charge of 80 lbs. of carbonate of potassium about 100 lbs. of animal matter having the highest amount of nitrogen are required, or a proportionate quantity of leather cuttings. This is several times more than is contained in the comparatively small proportion of ferrocyanide obtained from the charge; but the loss is enormous, and is incurred by the evolution of large quantities of nitrogen and ammonia during the calcination. The following is an analysis, by TENNENT, of the prussiate cake:—

		Per Cent.
Soluble.	Cyanide of potassium,	10·95
	Carbonate of potassium,	29·30
	Hydrate of potassium,	10·93
	Sulphate of potassium,	6·62
	Chloride of potassium,	1·58
	Sulphate of calcium,	11·42
	Volatile matter,	18·00
Insoluble.	Iron, Sulphide of iron,	8·56
	Carbonate of calcium,	·72
	Silica,	3·30
		101·38

In this analysis no notice is taken of soda; but the method which the analyst adopted must have caused soda to be recorded as potash. The fused mass is ladled from the pots, cooled slowly, and, when cold, lixiviated with water moderately heated. A sample of the insoluble matter, or "prussiate waste," was found to have the following composition :—

		Per Cent.
Soluble.	Ferrocyanide of potassium,	·391
	Carbonate of potassium,	1·054
	Sulphate of potassium,	traces.
	Sulphite of potassium,	
	Thiosulphate of potassium,	
	Sulphide of potassium,	
	Chloride of potassium,	
	Carbonate of sodium,	·150
Insoluble.	Carbon,	5·405
	Nitrogen,	·086
	Sulphide of iron,	2·996
	Sulphide of calcium,	·570
	Magnesia,	·071
	Alumina,	·621
	Silica,	·977
	Water,	87·679
		100·000

It is manifest, however, that the proportion of water must vary very largely. The solution from this insoluble matter has a specific gravity of about 1·1, but is further concentrated to about 1·27, and, after being cleared by settling, transferred to cast-iron crystallizing vessels, in which the "prussiate scale," or first crop, is produced, and of which the following is an analysis by TATLOCK :—

	Per Cent.
Ferrocyanide of potassium (crystals),	97·23
Sulphate of potassium,	·02
Sulphite of potassium,	·34
Thiosulphate of potassium,	trace.
Sulphide of potassium,	absent.
Chloride of potassium,	trace.
Carbonate of potassium,	·54
Insoluble,	·03
Water,	1·84
	100·000

The scales are dissolved in hot water and the solution recrystallized, pieces of twine being placed in the liquor as "nuclei," and the fluid allowed to cool as slowly as possible, with the object of obtaining large and transparent crystals. The mother liquors are either used for lixiviating fresh "cake," or they are boiled down to about 1·35 specific gravity, during which they deposit the greater part of the ferrocyanide they contain in the form of small crystals, which are purified by recrystallization, and the resulting lyes evaporated to dryness and calcined, when a residue called "recovered ash," or "blue salts," is obtained, containing from 60 to 70 per cent. of carbonate, with variable quantities of sulphate, sulphite, thiosulphate, and sulphide of potassium, some hydrate or carbonate of sodium, and always a considerable quantity of silica. This recovered alkali is of course available for further use. The following table (XXXV.) gives analyses, by TATLOCK, of two samples of commercial ferrocyanide of potassium :—

TABLE XXXV.

	1.	2.
Ferrocyanide of potassium (crystals),	99·88	99·80
Sulphate of potassium,	·06	·08
Chloride of potassium,	trace	trace
Carbonate of potassium,	·08	·09
Thiosulphate of potassium,	absent	absent
Sulphide of potassium,		
Insoluble,		
Water,		
	100·02	99·97

In this country, and on the Continent, a close reverberatory furnace (and recently in Germany a gas-generating furnace) has been tried, on the hearth of which is a thick iron pan about 5 feet in diameter, capable of holding a working charge of from 3 to 5 cwts. of material; and on the Continent a portion of nitrogenous charcoal or torrefied animal matter is generally mixed with the fresh organic matters.

It has been frequently attempted to make the nitrogen of the air the source of the cyanogen of the ferrocyanide; but up to the present time without success. One of the most noteworthy efforts is that of Messrs. BRAMWELL and HUGHES, who in 1844 carried into practice processes based on the reactions observed by THOMPSON, FOWNES, YOUNG, RIEKEN, and DELBRUCK, and wrought out by POSSOZ and BOISSIÈRE, which were to the effect that when charcoal saturated with carbonate of potassium is heated to whiteness in a current of nitrogen, cyanide of potassium is produced. After an expenditure of several thousand pounds, however, the scheme was abandoned, and the process now followed is the same in principle as it was seventy years ago.

Applications.—Ferrocyanide of potassium is employed in dyeing, chiefly for producing blues on cotton; much of it is also used in the preparation of the ferricyanide and cyanide. It is largely consumed in the manufacture of Berlin blue, and in the case-hardening of small steel articles.

Properties.—The pure salt crystallizes in the form of beautiful amber-yellow deeply truncated octahedra of the quadratic system, more of the apex being generally wanting on one side than on the other, giving the crystals the appearance of tables. It has a saline and slightly bitter taste, and aperient properties, although not poisonous. Heated to 100° C. it loses the whole of its crystalline water, and at a little over a red heat it melts, giving off nitrogen, forming cyanide of potassium, and depositing carbide of iron; if air be admitted, however, cyanate of potassium (KCNO) is also formed. Heated with five or six times its weight of strong sulphuric acid, sulphate of ammonium, sulphate of iron, sulphate of potassium, and carbonic oxide are produced, thus :—

$$K_4FeC_6N_6 + 6H_2O + 6H_2SO_4 = 3(NH_4)_2SO_4 + FeSO_4 + 2K_2SO_4 + 6CO.$$

If much water be present, however, hydrocyanic (prussic) acid is evolved, and in the cold, dilute acids liberate hydroferrocyanic acid. The crystals when exposed to light decompose superficially, giving off hydrocyanic acid, forming Prussian blue,

and becoming alkaline; and the aqueous solution is also slowly altered when long boiled, ammonia being evolved, and the fluid acquiring an alkaline reaction. It dissolves in 4 parts of cold and 2 parts of boiling water. The following tables (XXXVI. and XXXVII.), by SCHIFF, give the proportions of the salt in aqueous solutions of different densities, and the amounts dissolved by water at different temperatures.

TABLE XXXVI.

Quantity of Crystallized Ferrocyanide of Potassium in 100 *Parts of Water at Different Temperatures.*

Specific Gravity.	Per Cent. of $K_4FeC_6N_6 \div 3H_2O$.	Specific Gravity.	Per Cent. of $K_4FeC_6N_6 \div 3H_2O$.
1·0058	1	1·0669	11
1·0116	2	1.0734	12
1·0175	3	1·0800	13
1·0234	4	1·0866	14
1·0295	5	1·0932	15
1·0356	6	1·0999	16
1·0417	7	1·1067	17
1·0479	8	1·1136	18
1·0542	9	1·1205	19
1·0605	10	1·1275	20

TABLE XXXVII.

Solubility of Crystallized Ferrocyanide of Potassium in 100 *Parts of Water at Different Temperatures.*

Temperature.	Parts of $K_4FeC_6N_6 \div 3H_2O$ Dissolved.
Degrees C.	
12·2	27·8
37·7	65·8
65·5	87·6
96·3	90·6

Ferrocyanide of potassium shows the following behaviour with metallic salts in solution:—

Iron (ferrous),	white precipitate turning blue by oxidation.
Iron (ferric),	deep blue.
Copper,	brown.
Lead,	white.
Aluminum,	white (slowly).
Zinc,	white.

FERRICYANIDE OF POTASSIUM, $K_6Fe_2C_{12}N_{12}$, or $K_3FeC_6N_6$. Synonyms, Red Prussiate of Potash, Ferridcyanide of Potassium; *Prussiate Rouge de Potasse*, French; *Ferridcyankalium* or *Rothesblutlaugensalz*, German.

Manufacture.—This salt, discovered by GMELIN, is usually prepared by acting upon the roughly ground ferrocyanide by washed chlorine gas; but it can also be made by passing the latter through a solution of the same salt. The ferrocyanide in coarse powder is placed on wood or lead trays contained in a chamber, the gas being generated, usually, in lead vessels, by the action of hydrochloric acid on manganese ore. The substance acquires a deep orange-red colour, and the following reaction takes place:—

$$2K_4FeC_6N_6 + 6H_2O + Cl_2 = K_6Fe_2C_{12}N_{12} + 2KCl + 6H_2O.$$

As the water of crystallization thus liberated moistens the powder, it is better to previously expel a portion of it by heat. The product, a dilute solution of which should now give no blue coloration with weak solution of perchloride of iron, is dissolved in lead pans by open steam, and separated from the chloride of potassium by crystallization, pieces of string being placed in the fluid to serve as nuclei for the crystals. By evaporating the liquor a second crop of inferior crystals are obtained, the mother liquors of which may be employed in the preparation of TURNBULL'S blue with monosalts of iron; or it may be evaporated to dryness, and the compounds of potassium recovered in a crude form.

Applications.—Ferricyanide of potassium is chiefly employed in the preparation of TURNBULL'S blue, and in dyeing and calico printing, in which it is applied as a "discharge" in producing white patterns on a coloured ground. It is sometimes used in the state of powder, as made, without crystallizing.

Properties. — Ferricyanide of potassium crystallizes in splendid prisms of the monoclinic system, which are anhydrous, have a specific gravity of 1·845, and have a saline taste and aperient action, but are not poisonous. It is somewhat freely soluble in water, and from its high tinctorial power gives a strong yellow colour to that fluid, even when present in very minute quantity. When its aqueous solution is exposed to light or evaporated, it is partially converted into the ferrocyanide. The following table (XXXVIII.), by SCHIFF, shows the amount of ferrocyanide of potassium present in aqueous solutions of various densities, at 15° C.:—

TABLE XXXVIII.

Specific Gravity.	$K_3FeC_6N_6$, Per Cent.	Specific Gravity.	$K_3FeC_6N_6$, Per Cent.
1·0051	1	1·0891	16
1·0103	2	1·0952	17
1·0155	3	1·1014	18
1·0208	4	1·1076	19
1·0261	5	1·1139	20
1·0315	6	1·1202	21
1·0370	7	1·1266	22
1·0426	8	1·1331	23
1·0482	9	1·1396	24
1·0538	10	1·1462	25
1·0595	11	1·1529	26
1·0653	12	1·1596	27
1·0712	13	1·1664	28
1·0771	14	1·1732	29
1·0831	15	1·1802	30

The following table (XXXIX.), by WALLACE, represents the proportions of ferricyanide of potassium dissolved by water at different temperatures:—

TABLE XXXIX.

Temperature.	1 part of $K_3FeC_6N_6$ Soluble in Parts of Water.	100 Parts of Water Dissolve Parts of $K_3FeC_6N_6$.	Specific Gravity of Solution.
Degrees C.			
4·4	3·03	33·0	1·151
10·0	2·73	36·6	1·164
15·6	2·54	40·8	1·178
37·8	1·70	58·8	1·225
100·0	1·29	77·5	1·250
104·4	1·21	82·6	1·265

Ferricyanide of potassium is a powerful oxidising agent in presence of alkalies, ferrocyanide being formed and oxygen liberated, thus:—

$$2K_6Fe_2C_{12}N_{12} + 4KHO = 4K_4FeC_6N_6 + 2H_2O + O_2.$$

It therefore readily destroys vegetable colours.

CYANIDE OF POTASSIUM, KCN. *Cyanure de Potassium*, French; *Cyankalium*, German.

Preparation.—1. By heating potassium in cyanogen gas, when direct combination takes place; or in hydrocyanic acid vapour, when hydrogen is evolved. 2. By addition of hydrocyanic acid to solution of hydrate of potassium.

Manufacture.—When ferrocyanide of potassium, previously dried, is heated to dull redness in an iron crucible, cyanide of potassium is formed, along with carbide of iron, which separates from the melted product, while nitrogen gas is evolved, thus:—

$$K_4FeC_6N_6 = 4KCN + FeC_2 + N_2.$$

10 parts of ferrocyanide yield 7 parts of cyanide. For manufacturing purposes, however, the process known as RODGERS and LIEBIG'S is the one invariably followed. It consists in fusing, at a low red heat in an iron pot, 10 parts of the dried ferrocyanide of potassium with $3\frac{3}{4}$ parts of carbonate of potassium, which should be as free as possible from sulphate in order to avoid waste of cyanide in reducing the sulphate to sulphide. The product is 8·8 parts of cyanide mixed with 2·2 parts of cyanate of potassium, and the following is the change which occurs:—

$$2K_4FeC_6N_6 + 2K_2CO_3 = 10KCN + 2KCNO + 2CO_2 + Fe_2.$$

The action is complete when a sample of the fused mass taken out on an iron rod solidifies to a white opaque solid. The molten cyanide is then allowed to settle, and is poured into moulds or on a polished iron slab. According to HARRIS the proportions of carbonate of potassium should be varied according to the purpose to which the product is to be applied, that used for electro-gilding containing about 90 per cent. of pure cyanide of potassium, for ordinary electro-plating about 70 per cent., and for photographic purposes, from 40 to 50 per cent. Sometimes carbonate of sodium is employed instead of part of the carbonate of potassium.

Applications.—Nearly all the cyanide of potassium made is used in electro gilding and plating, and for photographic purposes. It is also applied in the reduction of some of the rarer metals from their ores.

Properties.—Cyanide of potassium, prepared as described above, is a white opaque solid with a crystalline fracture, the crystals being cubes; but those obtained from an aqueous solution are octahedra. It has a distinct odour of hydrocyanic (prussic) acid, arising from a slight decomposition by the carbonic acid of the air. It has an acrid and alkaline taste, and is a powerful poison. It is insoluble in *absolute* alcohol, but dissolves with great facility in water, and in aqueous solution it is decomposed, by boiling, into ammonia and formiate of potassium. It forms double salts with many metals, and particularly with silver, which are soluble in excess of alkali and of the cyanide—a property on which its usefulness in electro gilding and plating depends.

POTASSIUM BICHROMATE, $K_2Cr_2O_7$ or $K_2O,2CrO_3$. Synonyms, Bichromate of Potash, Bichrome; French, *Bichromate de Potasse;* German, *Zweifach Chromsaures Kali.*

This salt crystallizes in tables, of a beautiful red colour, which contain no water of crystallization, and fuse at a red heat. At a very high temperature it is decomposed into neutral chromate of potassium, oxygen, and oxide of chromium, which is in the crystalline condition, and sometimes used for razor strops and polishing purposes.

According to KREMERS, 1 part of bichromate of potash is soluble in—

20·14	parts of water at	.....	0° C.
11·81	" "	.....	10
7·65	" "	.....	20
3·43	" "	.....	40
1·98	" "	.....	60
1·37	" "	.....	80
·98	" "	.....	100

On account of its ready solubility in boiling water, it crystallizes well from a hot solution.

Bichromate of potash is made exclusively from chrome iron ore—a mineral which is regarded as having essentially the composition $FeOCr_2O_3$, but which almost invariably contains considerable quantities of alumina, magnesia, and silica. The ore is found in Russia, Turkey, Greece, North America, Shetland, and various other parts of the world, embedded in serpentine or some other mineral rich in magnesia. It is valuable only on account of the oxide of chromium which it contains, and this constituent varies in the ore used for manufacturing purposes from about 35 to 60 per cent. The following analyses, by CLARK, show the composition of average samples of shipments of chrome ores of various qualities:—

	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Oxide of chromium,	57·00	52·60	46·02	40·40	34·40
Alumina,	14·00	13·19	14·90	25·09	19·09
Protoxide of iron,	12·00	14·14	16·07	14·14	14·14
Lime,	·67	trace	trace	·67	·67
Magnesia,	15·00	14·72	15·85	13·83	20·90
Silica,	1·60	4·80	7·25	6·00	10·80
Water,	—	·70	·20	—	·30
	100·27	100·15	100·29	100·13	100·30

The amount of oxide of chromium in chrome ore may be determined either by precipitation or volumetrically.

Precipitation Process.—The finely pulverized ore is heated in a platinum crucible with about 10 times its weight of bisulphate of potassium, at first cautiously, and finally over a gas blow-pipe. When the fusion is calm, about twice its weight of ignited carbonate of sodium is added, and then an equal quantity of a mixture of nitrate of potassium and carbonate of sodium, and the fusion is continued over the blow-pipe for at least half an hour, that complete oxidation may take place. The fused mass is then boiled with water, to extract the chromate that has been formed; and the insoluble matter, which consists principally of oxide of iron,

magnesia, and any undecomposed ore, is filtered off and dissolved in hydrochloric acid, to ascertain whether all the ore has been decomposed. Any insoluble matter must be filtered off, and subjected to the same treatment as the original ore; the soluble in water being added to that obtained by the first fusion. To the yellow chromate solution, a considerable quantity of chloride of ammonium and a little carbonate of ammonium are added, and the solution is evaporated to small bulk, to insure the complete separation of the alumina and silica. The solution, from which the alumina and silica have been removed by filtration, is then acidified with hydrochloric acid, and the chromic acid is reduced with sulphurous acid or sulphite of sodium. When reduction is perfect, ammonia is added in slight excess, and the solution is boiled till it has no longer any smell of ammonia. The dingy green precipitate of oxide of chromium which separates is well washed with boiling water, by decantation; and as it is very difficult to get rid of the sulphates, it is advisable to redissolve and reprecipitate the oxide of chromium, and wash with boiling water till the washings cease to give the slightest indication of sulphuric acid. The precipitate is then dried, ignited, and weighed as oxide of chromium.

As the precipitation method, even when conducted with the greatest care, has a tendency to give too high results, the amount of oxide of chromium may be determined, with greater convenience and accuracy, by CLARK'S volumetric process.

Volumetric Process.—The finely-pulverized ore is heated for about an hour, over a Bunsen burner, in a platinum crucible, with about 6 times its weight of an intimate mixture of 5 parts of hydrate of sodium and 3 parts of calcined magnesia; oxidation begins at once, and is practically complete in less than an hour. The crucible is allowed to cool, and the contents are washed into a basin, as far as possible, with water, and afterwards with dilute sulphuric acid, which must be perfectly free from nitric acid; an additional quantity of dilute sulphuric acid is then added, and heat applied, when everything, except perhaps a little silica, should dissolve. To the clear solution a weighed quantity of sulphate of iron and ammonium, of known strength, and more than sufficient to reduce all the chromic acid, is added, and the excess of unoxidised iron is estimated with a weak standard solution of bichromate of potassium, and the amount of oxide of chromium in the ore is calculated from the iron which has been oxidised. Should any of the chrome ore escape decomposition, it can be separated by filtration, after the estimation of the chromic acid, and be again fused with a mixture of magnesia and hydrate of sodium.

Bichromate of potash was at one time made by heating chrome ore with nitrate of potash, and afterwards by fusing the finely-pulverized mineral in a reverberatory furnace with carbonate of potash, by which means the oxide of chromium in the ore was converted into chromate of potash. STROHMEYER added lime to the carbonate of potash, to reduce the quantity of alkali required, and assist the oxidation, by preventing the mass from becoming fluid; and JACQUELIN, to prevent the loss of potash by volatilization, which takes place even in presence of lime, recommended that the finely pulverized chrome ore should be furnaced with lime, the chromate of lime thus formed treated with water and sulphuric acid, to convert the chromate of lime into bichromate of lime, and the addition of carbonate of potash, to convert the bichromate of lime into bichromate of potash. Dr. A. W. HOFFMAN, in his "Bericht über die Entwickelung der Chemischen Industrie," gives the following description of the manufacture of bichromate of potash communicated to him by ROWLAND ATCHERLY:—

"The chrome ore—best Turkish or Asiatic, as it contains a comparatively large quantity of oxide of chromium, and very little oxide of iron or silica—after it has been stamped, is ground in horizontal mills, and then passed through a sieve which has 80 openings to the square inch. The fine powder is then carefully mixed, in cylinders which revolve on a diagonal axis, with potash lime, which is prepared on the spot from burned Irish limestone and a solution of carbonate of potassium, in the proportion of 7 cwts. of lime to $2\frac{1}{4}$ cwts. of carbonate of potassium. The carbonate of potassium employed should be free from chloride, as this would interfere with the subsequent crystallization of the bichromate. The limestone should contain very little combined silica, and be free from sodium and magnesium.

"The potash lime, which, when properly prepared as above described, has a thoroughly dry appearance, is mixed with $4\frac{1}{2}$ cwts. of pulverized and sifted ore. The weight of the mixture thus obtained forms the charge for the succeeding process of calcination. The furnace employed has a flat hearth, 9 feet long and 6 feet broad. The space between the roof and the floor is about 2 feet 6 inches, and narrows gradually to 18 inches at the outlet. The flame is blown down upon the hearth by means of a jet of steam. The hearth is provided with two fire-clay doors, by which the charge is introduced, and spread out in a layer, about 2 inches deep, over the half of the hearth lying nearest the fire. The furnace is heated before the operation is begun. The draught should not be too strong nor the fire crackle, nevertheless care must be taken that the mixture is exposed to an oxidising flame. The temperature at which the calcination takes place is a bright red heat. Every quarter of an hour the mass is turned over with an instrument like a plough, and in this way a new surface is exposed to the action of the flame. After two hours the workman pushes the mass gradually on to the other half of the hearth, and a new charge is introduced into the space which has been vacated. The turning over every quarter of an hour is continued. When the process of calcination has been properly conducted, it should be finished in four hours. The proportion of oxide of chromium converted in this way into chromic acid,

is said to be not less than 90 per cent. of the entire amount of oxide contained in the ore. The material, when properly calcined, has a greenish yellow colour. It is interspersed with hard lumps, which have a bright yellow fracture, and it consists of the chromates of potassium and calcium, free lime, silicate of potassium, and oxide of iron. When cool, the mass is broken up into coarse powder, and put into wooden lixiviating vats, where it is treated with a hot saturated solution of sulphate of potassium, which converts the chromate of calcium into chromate of potassium, with the formation of sulphate of calcium. The lixiviating vats are so placed that the solution of sulphate of potassium, after it has passed through one vat, flows into the rest, so that finally a saturated solution of chromate of potassium is obtained, from which the sulphate of calcium in suspension is allowed to deposit in deep vessels. The clear fluid is now brought to the decomposing vats, which are lined with lead; a sufficient quantity of English sulphuric acid, diluted with twice its volume of water, is then added, and the mixture allowed to cool. Now as a solution of chromate of potassium, saturated at 16° C., contains nearly 1 part of salt to 2 of water, whilst the bichromate requires 10 parts of water for its solution, it follows, that when a saturated solution of the chromate is converted into bichromate, three-fourths of the bichromate formed will be obtained as a precipitate on cooling. The precipitate is collected and then recrystallized, whilst the mother liquor, which contains sulphate of potassium, is used for the lixiviation of the calcined mass. The bichromate crystallizes best in deep iron vessels, out of a solution having a specific gravity of 1·120. Strings are introduced into the solution, and the temperature is kept about 21°."

Attempts have been made to prepare the chromate of potash direct from chloride and sulphate of potassium. According to Tilghmann, when chrome ore in a fine state of division is mixed with chloride of potassium, and subjected to the action of air and superheated steam, the oxide of chromium is converted into chromate of potash, and the same product is obtained by calcining chrome ore with a mixture of lime and sulphate of potash, and treating the product in the usual way.

In 1875 Townsend took out a patent for improvements in the manufacture of chromates, which consist, essentially, in the use of a mixture of lime and magnesia instead of lime; and in 1876 Clouet patented a process, in which he employs gas retorts instead of reverberatory furnaces, and carbonate of magnesium instead of lime, and he uses the insoluble in water for the calcination of a fresh quantity of ore.

The manufacture of bichromate of potash is carried on principally in this country, where there are in all four works—three in the neighbourhood of Glasgow, belonging to Messrs. J. & J. White, Stevenson, Carlile, & Co., and the Eglinton Chemical Co.; and the fourth that of Messrs. W. J. Norris & Brother at Sowerby Bridge, near Manchester. In 1868, according to Persoz, the total annual production of bichromate of potash throughout the entire world was about 3000 tons; but the consumption has increased so rapidly that the production in the United Kingdom alone amounts now to about 10,000 tons per annum.

Bichromate of potash is extensively applied as an oxidising agent, especially in dyeing and in the manufacture of alizarin; and it is used in the preparation of various yellow, orange, red, and green colours, and in the bleaching of palm oil.

Chromate of Potassium, K_2CrO_4. Synonyms, Yellow Chromate of Potash; German, *Chromsaures Kali;* French, *Chromate de Potasse.*

This salt is formed in the manufacture of the bichromate, and it may be obtained by heating the bichromate to a temperature sufficient to decompose it into oxide of chromium and chromate of potassium, or by adding the proper quantity of potash to a solution of the bichromate. At the ordinary temperature, chromate of potassium is soluble in about 2 parts of water, and the solution has an alkaline reaction, a strong yellow colour, and a persistent bitter taste. It is poisonous even in small doses. Chromate of potassium crystallizes in yellow six-sided pyramids, like sulphate of potash, with which it is isomorphous, so that these two salts can crystallize together in all proportions.

Bitartrate of Potassium, $KHC_4H_4O_6$. Synonyms, Bitartrate of Potash, Cream of Tartar, and (in the crude state) Argol; *Tartrate Acide de Potasse*, French; *Saures Weinsaures Kali*, or *Weinstein*, German.

Manufacture.—This substance exists in comparative abundance in the juice of every variety of grape, the proportion varying from ·5 to 2 grams. per litre, according to circumstances. During the fermentation of the grape juice or "must" this is deposited gradually as the proportion of alcohol increases, by reason of its insolubility in that substance; the result being, in the case of red wines, a plentiful incrustation of a reddish colour, and in that of the white varieties a less abundant product of a paler colour. These constitute the "argols" of commerce, which always contain more or less bitartrate of calcium—an impurity which even remains to some extent in the "cream of tartar" produced from them by refining. The following table (XL.) shows analyses of the crude bitartrate, viz.:—

TABLE XL.

	Red.	White.
Bitartrate of potassium,	84·26	88·38
Tartrate of calcium,	5·90	3·94
Sulphate of potassium,	trace.	trace.
Chloride of potassium,	trace.	trace.
Colouring matter, &c.,	9·00	7·04
Moisture,	·84	·64
	100·00	100·00

A further quantity of the crude substance is deposited in the vats and casks, and even in the bottles containing the wine, forming the well-known crust. Sometimes sulphate of calcium is added to the grapes before they are pressed, with the object

of getting the wine to clarify quickly, sulphate of potassium remaining in solution, and tartrate of calcium falling down insoluble and carrying with it most of the suspended particles; but by this treatment the greater part of the bitartrate is destroyed. The crude argol is refined by repeatedly dissolving in boiling water and cooling, when crystals are obtained of a higher degree of purity at each operation, the liquors in the last process being treated with albumin, which coagulates, carrying the impurities with it to the surface, from which they are skimmed off. The following table (XLI.) gives analyses of some samples of commercial cream of tartar, by Tatlock:—

TABLE XLI.

	1.	2.	3.	4.
Bitartrate of potassium,.....	91·2	91·1	90·8	92·6
Tartrate of calcium,.....	8·4	8·3	7·8	6·6
Moisture,.....	·2	·2	1·6	7
	99·8	99·6	100·2	99·9

The proportion of tartrate of calcium in these four samples is higher than usual; it should not exceed 5 per cent., as its presence in large quantity is objectionable on account of the property which it has, in presence of moisture, of gradually decomposing the bitartrate of potassium.

Probably not less than 3500 tons of argol are annually imported into this country at the present time from the wine countries of Europe, of which a large proportion is shipped from Naples. The greater part of this, however, is really wine-lees used in the manufacture of tartaric acid.

Applications.—Both "tartar" (crude) and "cream of tartar" (refined) are largely employed in dyeing cochineal and lac-dye scarlets on wool, and the crude for the manufacture of tartaric acid.

Properties.— Bitartrate of potassium is a white crystalline substance, having a sour but not disagreeable taste. When heated in a close vessel it is decomposed, forming the mixture of carbonate of potassium with carbon in a minute state of division, known as "black flux." It is slightly soluble in cold, but dissolves to a considerable extent in boiling water. The following table (XLII.), by Brande and Wardenburg, shows its solubility in water at different temperatures:—

TABLE XLII.

Parts of Water in which 1 Part is Soluble.	Temperature.	Parts of Water in which 1 Part is Soluble.	Temperature.
	Degrees C.		Degrees C.
240·0	10	47·4	37·5
234·6	15·5	37·8	50
183·67		32·4	62·5
184·71	18·75	22·0	75
202·10		17·7	87·5
89·0	25	14·3	100

Uses of Potash in Agriculture.—Although it is now universally admitted that potassium in some form of combination is an essential element in the mineral food of plants, and that it should therefore be present in manures, agriculturists have scarcely yet awakened to a perception of its momentous importance in that respect. While it is quite true that its compounds are introduced to some extent in manufactured manurial substances—particularly such as are employed in the cultivation of sugar-beet, sugar-cane, coffee, hops, and tobacco — in most instances these are made to occupy but a subordinate place, whereas they are probably the most necessary part of plant food. This has partly arisen, no doubt, from the hitherto comparatively high price of these compounds—an obstacle which will probably be to a considerable extent removed by the still greater development of the working of the gigantic potash deposits of Stassfurt and Douglashall. It is manifest that the enormous quantities of potassium compounds removed from the soil by every variety of crop must ultimately exhaust it, however rich it may have been originally, if they are not replaced. Virgin soils of course frequently contain a considerable proportion, derived from the rocks which, by disintegration, gave rise to them; but although this is in a state assimilable by plants, and quite available for their nutrition, it is soon taken up and removed, and unless replaced, the soil must become impoverished; and it is not to be expected that it could be eliminated from a state of combination in which it is insoluble as fast as it would be required by the growing vegetable, and which without a sufficient supply could not thrive. The researches of Vobbe, Schrœder, and Erdmann, of the Academy of Agriculture near Dresden, made at the instance of the Saxon Government, prove the importance of the salts of potassium in vegetation; and their conclusions are fully borne out by the investigations of Heppe, of Leipzig, as well as by those of Way and Ogston, Richardson, and others. Numerous experiments recently made in France, by order of the Minister of Agriculture, on the application of potassium salts in the culture of the vine, are most conclusive in showing that it is of inestimable value for that purpose; and the recent employment of sulpho-carbonate of potassium as a remedy for phylloxera in vines may stimulate the production of the carbonate from various sources.

There were grown in Germany in 1875 over 4,000,000 tons of sugar-beet, which drew from the soil about 30,000 tons of potassium salts; and 50,000 tons more of the latter were withdrawn by the potato crop in the same country, only one half of this amount being returned to the ground in the farm-yard manure; while it is computed that, in France alone, the wine crop carries from off the soil 16,000 tons of potassium salts every year.

The following table (XLIII.), compiled from Liebig and Kopp's reports and other sources, in which is stated the amount of potash in the ash of a number of vegetable substances, will show its importance as an ingredient of plant food. These are merely given as examples; the proportions must, of course, vary within certain limits, according to circumstances:—

TABLE XLIII.

Vegetable.	Potash (K_2O) Per Cent. in Ash.	Analyst.
Wheat (grain),	23·18	Weber.
Oats "	24·30	Way & Ogston.
Barley "	31·55	"
Rye "	33·83	"
Potato (roots),	63·24	Griepenkerl.
White cabbage,	54·21	Stammer.
Lettuce,	46·07	Richardson.
Turnip (roots),	36·16	Way & Ogston.
Peas (seeds),	42·64	Frankenfelde.
Kidney beans (seeds),	36·83	Richardson.
Parsnip (roots),	36·12	"
Leek (bulbs),	32·35	"
Celery,	43·17	"
Sprouts,	21·89	Way.
Asparagus,	22·85	Schlienkamp.
Cauliflower,	34·39	Richardson.
Rhubarb (stem),	59·59	"
Radish (root),	21·96	"
Broccoli (leaves),	22·10	"
Spinage,	9·69	"
Grape (Algerian),	41·24	Tatlock.
Carrot (root),	37·55	Frankenfelde.
Apple,	35·68	Richardson.
Pear,	54·69	"
Strawberry,	21·07	"
Cherry,	51·85	"
Jerusalem artichokes (roots),	55·89	Frankenfelde.
Fig (fruit),	28·36	Richardson.
Walnut (kernel),	31·11	"
Cucumber,	50·06	"
Orange (entire),	38·72	"
Chestnut,	39·36	"
Plum,	59·21	"
Lemon (entire),	29·49	Tatlock.
Pine apple,	49·97	Richardson.
Mangold wurzel,	23·54	Frankenfelde.
Clover (red),	18·44	"
Hay,	11·93	Hubert.
Italian rye grass,	12·45	Way & Ogston.
Vetches (seed),	39·10	Sprengel.
Hops,	24·88	Way & Ogston.
Rape (seed),	28·94	Weber.
Flax (straw),	43·42	Meyer & Brazier.
Linseed,	34·17	Way.
Rye grass,	28·99	Way & Ogston.
Tea (Himalayan),	39·22	Zöller.
Coffee (Ceylon),	55·10	Graham, Stenhouse, and Campbell.
Chicory (Yorkshire),	33·48	"
Maize,	30·74	"

It is manifest that if potash is not supplied to the extent to which it is abstracted, the crop must suffer accordingly, and the yield will diminish. Plants have the power, however, to some extent, of substituting one kind of mineral food for another; and the more closely bodies resemble each other in their chemical characters, the more readily will they replace each other, in the ratio of their chemical equivalents, in the growing plant. It seems to be established beyond doubt that the sulphate of potassium has a higher agricultural value than the chloride, and for that reason it is generally preferred to the latter in artificial manures.

Recently, potash in the form of kainit—the double sulphate of potassium and magnesium found in the Leopoldshall mine—has been applied, in conjunction with dissolved bones and nitrate of soda, to a large extent in the reclamation of peat lands in Holland and Germany, the operations in all cases having been attended with strikingly marked success.

The physiological action of potassium compounds is peculiar. In small doses they are stimulating, but in excessive quantities they are unmistakeably poisonous, paralyzing the action of the heart; and yet the analysis of animal tissues shows the absolute necessity of an abundant supply of potash. Tatlock found in the ash of ox-flesh 43·36 per cent., and in that of cow's milk 16·56 per cent. of the last-named substance.

Detection and Estimation of Potassium.—This metal may be detected by means of the spectroscope, its spectrum showing a dull band in the red, and a faint, but very distinct, line in the violet. In the absence of sodium it also communicates a violet tint to non-luminous flames. Its proportion is usually determined by converting it into, and weighing it as, potassio-platinic chloride; but while it is admitted by all chemists that this method gives results which, in point of accuracy, leave nothing to be desired, much controversy has arisen with regard to the best way of applying it. Nearly all transactions in potassium salts being now based on the strength as ascertained by analysis, the subject is one of great commercial importance, and in 1875 a Committee was appointed by the British Association for the Advancement of Science to investigate the subject. The following extract from the Report of the Committee, based on the results of many experiments, will show the condition in which they found the question, and the conclusions at which they arrived.

"The following modifications of the general process have been employed by the Committee, with the view of testing their comparative accuracy under various conditions likely to occur in practice. The information forming the basis of the experiments was chiefly communicated to the Committee during last year, and to a great extent was incorporated in the Report presented at the Bristol Meeting.

"*Modification I.*—Essentially the process of Professor Fresenius, described in his 'Manual of Quantitative Analysis,' being shortly as follows:—The solution of mixed chlorides of potassium and sodium, freed, if necessary, from calcium, magnesium, and sulphates, was evaporated nearly to dryness with excess of solution of platinic chloride. (In many of the experiments a considerable excess of platinum was employed beyond the quantity required to convert both the alkali metals into chloro-platinates.) The evaporated solution was then treated with alcohol of about 80 per cent., transferred to a small filter, washed with alcohol of 80 per cent., and carefully dried. The bulk of the precipitate was then transferred to a weighed capsule, dried at 100° C., and weighed. The filter with from 1 to 3 milligrammes of adherent precipitate was ignited, the weight of the filter-ash (0·0004 gram.) subtracted, and the residue of Pt + 2KCl calculated to 2KCl + $PtCl_4$, the amount thus obtained being added to the main quantity.

"*Modification II.*—The above process, with the following precautions, was recommended by Dr. Fresenius in a communication to this Committee:—To make sure not to keep any chloride of sodium

along with the chloride of potassium and platinum, I first extract the chloride of platinum and sodium with spirits of wine of 80°, and then wash the chloride of platinum and potassium with a few c.c. of water, drop by drop; then I evaporate this solution, adding a little chloride of platinum, treat the small precipitate again with spirit of wine, and add the small quantity of chloride of platinum and potassium to the bulk.

"*Modification III.*—The third modification is that of Drs. Frank and Berrand of Leopoldshall. These chemists employ only about 0·2 gram. of the potassium salt, and manipulate like Fresenius; but they wash the precipitate with alcohol of 98 per cent., which is practically absolute. They dry the precipitate at 110° C.

"*Modification IV.*—The fourth modification is that of R. R. Tatlock, who thus describes it in his communication to the Committee:—A portion of the solution, equal to 10 grains of the original sample, is delivered into a small basin, diluted with 400 grains or so of water, and acidified slightly with hydrochloric acid. About 500 grains of platinic chloride solution (containing at least 25 grains of platinum) are added, and the fluid evaporated nearly to dryness on a water bath. A few drops of water are then added to the residue, and the evaporation repeated to expel the excess of hydrochloric acid. About 50 grains more of the strong platinic solution are mixed with the precipitate, and the whole stirred well, and set aside in a cold place for at least an hour, with occasional stirring. The precipitate is then thrown on a very small filter (unweighed), the basin rinsed out with about 10 drops more of the platinum solution, and the precipitate on the filter washed with 10 or 15 drops more. The basin and the filter and contents are then washed with the smallest possible quantity of alcohol of 95 per cent. strength, and dried at 100° C. The dried precipitate is transferred as completely as possible to a small capsule, in which it is further dried until it assumes a distinct orange colour, and weighed. The filter, with a trace of adhering precipitate, is ignited on a crucible lid, and the residual metal, with its corresponding chloride of potassium, calculated to potassio-platinic chloride, and the weight added to that of the precipitate.

"From the above description it will be seen that the chief points of difference in the processes are as follow:—

"Fresenius (Process I.) uses moderately strong alcohol (80 per cent.) for washing the precipitate, but in his modified process he subsequently uses a few centimetres of water, and recovers any potassium salt thus dissolved.

"Frank and Berrand wash with absolute alcohol.

"Tatlock washes first with strong solution of platinic chloride, and then with strong alcohol.

"From a general consideration of the foregoing researches on the determination of potassium, as chloro-platinate, it appears that—

"1. Potassium in the form of pure chloride can be determined with great accuracy by precipitation as chloro-platinate. If a large excess of platinum solution be employed, and alcohol only used for washing the precipitate, the results have a tendency to exceed the truth. By avoiding the use of a large excess of platinum solution more accurate results are obtained. If a small volume of platinum solution be employed in the first instance for washing the precipitate (as recommended by Tatlock), and the washing then completed with alcohol in the usual way, the results are very accurate. Potassium chloro-platinate appears to be practically insoluble in a concentrated solution of platinic chloride.

"2. In presence of a considerable proportion of chloride of sodium, washing the precipitate with alcohol alone tends to give results in excess of the truth. If the precipitate be first treated with platinum solution the results are somewhat low, apparently owing to the solubility of the precipitate in solution of sodium chloro-platinate: the error increases with the amount of sodium, but is never very large, and a correction may be applied if desired.

"3. If Tatlock's method be employed there is no occasion to separate any sulphates, nitrates, or magnesium; but if the amount of chloride present is insufficient for the existence of all the potassium as chloride of potassium, the deficiency must be supplied by the addition of chloride of sodium or hydrochloric acid. The results obtained are in many cases very accurate, but have a tendency to be somewhat below the truth.

"4. There is practically no advantage in drying chloro-platinate of potassium at 130° C. rather than at 100° C.; the loss at the higher temperature was found not to exceed 0·07 per cent. of the weight of the precipitate, but it is probably governed by the conditions of precipitation.

"5. The Committee is of opinion that a preliminary washing of the precipitate of chloro-platinate of potassium with a solution of platinic chloride is a valuable modification of the usual process. As the method so modified is capable of direct application to the commercial salts of potassium, and does not necessitate the removal of sulphates, nitrates, or magnesium, the Committee considers that it deserves to be generally applied to the determination of potassium in commercial products containing it."

Various other methods have been proposed for the estimation of potassium. That of Schlœsing consists in treating the concentrated solution with perchloric acid, evaporating to dryness, and, after washing the residual perchlorate of potassium several times with alcohol, again evaporating to dryness, washing with spirit, drying, and weighing. There is no doubt that this process is capable of great accuracy, and separates potassium from sodium with much exactness. Carnot precipitates the potassium by means of a solution prepared by dissolving 1 part of subnitrate of bismuth in a few drops of hydrochloric acid, adding 2 parts of sodium thiosulphate and then a large excess of alcohol. A yellow precipitate is produced which is a double thiosulphate of potassium and bismuth; it is washed with alcohol, and the bismuth separated from it by dissolving in water, adding sulphide of ammonium, and weighing

as sulphide of bismuth. According to PESIER'S method of separating potassium from sodium, the mixed salts are converted into sulphates by evaporation to dryness with sulphuric acid, and calcining with a piece of carbonate of ammonium; the resulting mixed neutral sulphates dissolved in the smallest quantity of hot water; and the solution allowed to cool perfectly until crystallization is complete. The specific gravity of the mother liquor is then carefully taken, and if no sodium is present it should correspond exactly with that of pure sulphate of potassium; but the presence of the former, of course, adds to the density of the fluid, and from the difference in this respect the amount of sodium is arrived at by means of a table constructed for the purpose. There is a danger of error from supersaturation, but the results, considering this, are tolerably correct. The sodium salt must never be present, however, in large enough proportion to crystallize out.

POTTERY.—*Poterie*, French; *Steingut*, *Porzelan*, *Topfen*, German.—The potter's wheel is one of the most ancient mechanical appliances, and has remained unchanged for thousands of years. An Egyptian thrower of the time of the Pharaohs would, if he were resuscitated, be capable of at once taking a place in a modern pottery.

The most ancient specimens of fictile manufacture now existing are the sun-dried and kiln-baked bricks of Egypt and Assyria: next followed terra-cotta, an earthenware of a dull coarse appearance without any glaze. It is simply clay baked at a low temperature till it acquires a soft pale tint. The Romans burnt their bricks till they were of a deep red colour. Tiles came into use at a very early period; they were used for roofing purposes, and also for decorating walls, floors, &c. When used for ornamental purposes they were commonly glazed.

The tiles of the Egyptians of the sixth dynasty were glazed with a mixture of powdered silica and carbonate of soda from the soda lakes of Egypt—the "nitre" of the Holy Scriptures, but really natron; the colours were obtained by addition of metallic oxides. An oxide of copper produced the celestial-blue glaze. The green glaze is of a kindred nature with the blue; and manganese, gold, silver, tin, &c., produced the violet, yellow, white, and red hues.

The Assyrians applied a glaze or enamel to some of their kiln-dried bricks on one face only; the colours used were blue, yellow, white, red, and black. The Assyrians were great writers upon tiles, and they also employed cylinders and prisms for the same purpose. Whole libraries of these imperishable tablets have been found.

Tiles were extensively used by the Greeks and Romans, both for roofing and for the flues of baths, and also in the construction of many of their tombs.

Flue-tiles, which are necessarily hollow, almost invariably measure 16½ inches in length by 6½ inches in width and 5 in depth. They have their surfaces scored either with wavy lines or more systematic patterns.

Drain-tiles, or terra-cotta pipes, are larger than those used for flues.

Wall-tiles are large thin squares of terra-cotta, and they generally were decorated on one side with incised figures and patterns.

Floor-tiles were extensively used by the Romans in the construction of their *hypocausts* and *suspensuræ*. When the builders of a Roman villa desired to warm a room, they constructed a warm air chamber below it, supporting the floor upon a number of stone pillars, or of piers of square tiles set out at equal intervals. Upon these a series of larger tiles were laid, and on these some not less than 18 inches square, until a continuous surface was obtained, on which the concrete for the pavement itself could be firmly laid. Tiles of the following dimensions are commonly found in the extant floors of Roman villas in England:—

For the piers, ...	7½	inches square.
For the second row, ...	13	"
For the third and last row, ...	18	"

Such tiles often show footmarks of the dog, goat, sheep, ox, and other animals, which have walked over the moulded clay before burning.

During the time of the Roman occupation of Britain immense quantities of the rougher sorts of pottery were manufactured, especially for sepulchral urns, in many parts of the country. These urns are plain, of simple and somewhat elegant form, of a grey or dull black colour, and generally ornamented with a broad band of crossed lines around the widest part of the vessel. They were generally burnt in a "smother kiln," so as to give them a dark hue; and were often made of coarse clays, little adapted for the potter's art. A better sort of ware, also of dark colour—in fact, nearly black—was made at Upchurch, in Kent, and along the banks and creeks of the Medway, where vast accumulations of Roman pottery have been discovered. At and below Castor, in Northamptonshire, the Durobrivæ of the Romans, and at Colchester, kilns, with potters' tools and finished vessels, have been found; but in these instances the ware is more varied in character, and of higher style as to decoration. A curious buff-coloured ware, ornamented with circles and undulating stripes in a thin red ferruginous pigment, have been found in kilns in the New Forest, England. So far as regards Romano-British pottery, we are able to affirm that it was of many different kinds, and was extensively manufactured here, although much was imported. Still we cannot assign a definite place of manufacture to all the different varieties which are known. Some of the tiles marked with the names of particular legions have been already described and allocated; on other tiles less intelligible letters appear. An interesting series found at Cirencester bears the name, ARVERI, preceded and followed by a small mark, which closely resembles the pointed spade still used in digging out potters' clays. Another series from the same Roman town shows a set of letters of which one, the last, changes as if following some regular order: the extant specimens read thus—TPFA, TPFC, TPFP.

The *red lustrous pottery*, commonly known as *Samian* or *Aretine* ware, from the celebrated potteries of Samos and Aretium, now Arezzo, in Tuscany, was in universal use wherever the Roman name was known in the ancient world. The period of the manufacture is considered to extend from the first to the third century of this era; and it would appear to have been produced in large quantities, as well in Roman Gaul and Germany, as in Italy and at Samos. The paste is of a rich sealing-wax red colour. The vessels vary considerably in form, but are rarely of a large size. They are thin and delicate in their structure: the red hue of the body or paste is derived from ferric oxide; the brilliant glaze is coloured red by the same means.

Examples of chocolate-brown, of black, of grey, and of yellow Samian ware, have been found both in this country and on the Continent. The ware, in fineness and character of paste, is at all events identical in these examples with the red ware which we have just been describing, and its decoration is similar; but it differs in colour, in the frequent absence of a glaze, and sometimes in the peculiar colours and even iridescence of the glaze. All these varieties are, however, very rarely met with: the same must also be said of a kind of Samian, in which the designs are sharply *incised* in the ware as with a sharp knife, not *impressed* by moulds or applied.

The black lustrous pottery of the Romans was made of any tenacious clay; it varies in colour from a rich deep black to a slate or olive hue. The black glaze was produced by smothering the fire of the kiln, so that carbon was deposited on the highly heated surfaces of the vessels, or the iron reduced to a lower state of oxidation.

The sepulchral mounds erected over the graves of deceased chieftains of the early European races have contributed many examples of the vases that were fabricated, both before and after the era of the Roman dominion, in countries beyond the limits of Italy and Greece. Urns and vases of various sizes and forms, generally without handles, are found in Anglo-Saxon tumuli. The rudeness of the greater number of the specimens of Anglo-Saxon pottery is, indeed, as remarkable as the tendency which it so generally exhibits to assimilate rather to the British than to the Roman types. The paste both of the Celtic and Saxon pottery is coarse, and consists of the clay found on the spot, which had not received much preparation, and had undergone a baking of only a very imperfect kind. The vessels are of a dull blackish-brown hue. They are generally of an urn shape, tapering towards the base, and having wide mouths with bevelled and overlapping lips; and their style of ornament consists, for the most part, of simple cords or bands of punctured zigzag and herring-bone work, intermixed with dots and small projecting bosses.

The Teutonic pottery, which is found throughout Germany, bears a considerable resemblance to that of the Anglo-Saxons. The urns are formed of a friable paste composed of clay and sand, intermixed with particles of mica, but the substance varies in colour in different localities. Like the Celtic pottery, many of the smaller vases have been modelled by the hand; but some of these, and the greater number of the larger urns, bear decided marks of having been turned upon the wheel.

For some centuries after the fall of the Western Empire pottery appears to have been confined to such simple vessels as are required for domestic purposes. And when at last improvements began to be gradually introduced, earthen vessels still continued for a long space of time to be esteemed simply as articles of present utility, so that but few specimens have been preserved. It is known that the Arabs employed lead glaze in the ninth century, and that the Moors introduced their plumbiferous glaze into Spain early in the thirteenth century, about which time its use seems to have spread into other countries. Stanniferous glazes were also brought into Europe by the Moors, and probably the use of both tin and lead in glazes or enamels became known in the West at about the same period.

As early as 527 the Saracens conquered Sicily, and adorned their great mosque at Palermo with coloured and enamelled tiles. In the ninth century they manufactured highly ornamental pottery and tiles in Majolica. In 1115 the Pisans carried off specimens of rich Moorish pottery, and thus helped to introduce the art into Italy.

In the thirteenth century Italian pottery already had a distinctive character. Under the Malatestas, lords of Pesaro, the manufacture assumed a more decorative and artistic aspect. A new process at this period was developed, upon which the subsequent ceramic operations of Italy were based. The red or other comparatively coarse and dark-coloured clay which formed the paste or actual body of the pottery, was first fired, or partly baked, and then, by immersion, it was covered with a thin coating of a composition formed of oxides of lead and tin, and of a very white earth procured from the territory of Siena; after this the ware was again placed in the kiln to receive its final firing. When the enamel was required to be more hard and white, the proportion of the tin was increased. The overlaying of an opaque white surface upon a coloured body of a totally different texture formed a process altogether new, which may be regarded as the basis of the celebrated *Majolica* ware of Italy.

Luca Della Robbia (1400–81), a goldsmith of Florence, after many experiments, arrived at the conclusion that an almost endless durability might be imparted to figures in clay by overlaying them with a thick glaze of tin combined with other mineral substances. About the year 1438 he introduced an opaque white, highly lustrous stanniferous enamel, which he was the first Italian to apply to terra-cotta. His earliest works are in white on a blue ground; but he subsequently introduced green, maroon, yellow, and violet. He appears, however, to have used those colours very sparingly, and to have retained his preference for white and blue. The

works of Luca Della Robbia, distinguished invariably by their simplicity and purity of style, consist of Madonnas and Scripture subjects, with architectural ornaments and glazed tiles. Many of his best productions still remain in undiminished beauty, as decorations in the walls, both external and internal, of the churches, monasteries, palaces, and other public and private buildings in Florence, where they were originally placed. Other specimens have found their way into museums: that at South Kensington possesses some characteristic examples.

The manufacture speedily secured great patronage, and designs were produced by artists of great skill. The manufactories of Urbino, situated in Castel-Durante and Faenza, are the places most celebrated for their Majolica. Besides its Majolica, Faenza produced bas-reliefs after the manner of Luca della Robbia; and this city, with Florence, was the first to adopt the beautiful white tin glaze, when the secret of its production had become known some years after the death of Luca. The term *Fayence*, now generally applied to all enamelled earthenware, and particularly to that of Italy, is supposed to have been derived from Faenza, in commemoration of the early use at that city, in its ceramic works, of the white Della-Robbian glaze. In several cities of the Papal States Majolica was made during the best periods of the art; and subsequently, at the close of the sixteenth century and throughout the century following, and even later still, the same manufacture was actively carried on in several parts of Italy. Majolica was produced in the sixteenth century both in Germany and France. Hirschvögel, an artist of Nuremberg, when travelling in Italy, visited Urbino in 1503; and having there learned the art of making this ware, he established a manufactory in his native city on his return: his works are ornamented in relief. At Nevers in France, also, a manufacture of Majolica was established by Duke Louis Gonzaga about the year 1570. About 1550 Bernard Palissy discovered for himself the enamels which enabled him to execute the remarkable ceramic works that are identified with his name. He had laboured through a memorable probation of fifteen years before success crowned his experiments. Thenceforward his career as an artist was one sustained triumph. He modelled exclusively from the fish of the Seine, from the fossil shells of the Paris basin, and from other natural objects found in the same localities. His enamels are hard and brilliant, and his hues rich and vivid. He employed a tin glaze, upon which his coloured enamels were laid.

The French Fayence, called Henri Deux ware, had a very brief period of manufacture. It was made at a private pottery belonging to the Chateau d'Oiron, near Thouars in Touraine, probably between the years 1524 and 1560. The paste is fine, of a creamy colour and ivory-like appearance. The decorations are mostly incised in delicate lines, and filled in with yellow, chocolate-brown, and black compositions. From the style and peculiarities of these coloured decorations, it is conjectured that the patterns used were bookbinders' moulds. Heads, mouldings, and other decorations in relief were also used upon this ware, particularly in the later examples. The paste is a hard white pipe clay, and the glaze gives it its warm yellow hue. The earlier designs are especially delicate in form and drawing, and show the *Renaissance* feeling of the period of manufacture. The dates given above are derived, partly from the evidence afforded by the pieces of this fabrique still extant, and partly by evidence which has been collected in the neighbourhood of Thouars. Of the former kind of proof we may cite the presence of the insignia of Francis I. upon the earlier pieces, and the arms of Henry II. upon the later and more elaborate works. Upon some of these there also appear the device (three crescents) of that monarch, or his initial (H) interlaced with the two Ds of Diane de Poitiers, Duchesse de Valentinois. It should be stated that this Henri Deux ware, or Fayence d'Oiron, was not made for sale, but for private use and for presents; the manufactory being the creation of the Gouffier family, owners of the Chateau d'Oiron. About 70 pieces of the elegant pottery survive, most of which are preserved in the public museums of France and England, or are in the hands of a few wealthy collectors of ceramic works. Their decorative effect may be compared to that of *niellos*, with accessories of *repoussé* and chased metal work; and they constitute some of the most delicate productions of fictile manufacture that are in existence.

Delft and other towns in Holland were early celebrated for their earthenware. Their subjects were for the most part copies, both in form and colour, of the old porcelain of Japan, with which the Dutch were familiar long before it was known to the rest of Europe. The clay found in the vicinity of Maestricht was mixed with marl or sand; and this was covered with a beautiful glaze having a blue tinge, which presented a smooth and even surface, and received paintings, in imitation of the Oriental, without impairing the distinctness of the colours. One curious branch of the Delft manufacture consisted of dinner services, of which the dishes and covers were made in the forms, and painted to resemble animals, birds, and vegetables, such as are usually served at table. The pseudo-Japan Delft ware flourished until the commencement of the eighteenth century, when it began to decline. The superiority of the wares of Wedgwood caused the Delft to be superseded, even in Holland, by pottery of English production.

The *Stoneware* of the Low Countries is a densely-baked earthenware, formed of clay mixed with sand, and glazed with salt. It exhibits, when broken, a close grey texture; it is somewhat vitreous, resists the action of fire, and is impermeable to liquids, even such as are of the most penetrating and corrosive nature. The stoneware of the Low Countries may be divided into common and fine. Both are usually ornamented with subjects in relief, and coloured; but the fine stoneware is distinguished by a more elaborate ornamentation as well as by the superior quality of its paste. The common stone-

ware appears to have been in general use towards the close of the sixteenth century. In many parts of Germany richly decorated earthenware was still made in the seventeenth century. The body or paste is often hard though dark in colour, covered with salt-glaze, and decorated with coloured fusible enamels and oil-gilding.

Although commonly spoken of as Grès de Flandres or Grès Flamand, much of the best stoneware was made in Germany, and not a little in France. Some of the early Beauvais specimens are beautiful in colour and decoration, as well as of excellent paste and glaze. The colours are chiefly cobalt blue and a manganese puce, which combine harmoniously with the finely-drawn incised ornaments and the encrusted flowers in grey. The manufacture of these wares, beginning in the earlier part of the fifteenth century, declined towards the middle of the seventeenth, giving way before the introduction of oriental porcelain and its Dutch imitations.

The few specimens of early pottery that have been found in England, and which may be considered to have been of home manufacture, are such as lead to the conclusion that before the seventeenth century this country was chiefly supplied with crockery ware from abroad. In some few instances foreign workmen settled in England, and thus their art became naturalized with them. Vessels, most of them tall and slender jugs, have been discovered in excavations in London which may be assigned to the fourteenth and fifteenth centuries, and were probably made in this country. The glaze used was obtained from lead. Amongst the productions of the seventeenth century, an English Delft may be considered to have occupied a prominent position. Dishes, plates, &c., were made at Lambeth, Fulham, Liverpool, Bristol, and in Staffordshire.

The Staffordshire Potteries now produce the great mass of the earthenware porcelain manufactured in this country. This district contains twelve lordships and three parishes, and constitutes the borough of Stoke-upon-Trent. The Romano-British ceramists, the Saxon *tile-wrights*, the Norman potters, and English potters, have successively occupied the same localities.

In 1686 Dr. ROBERT PLOT mentions Burslem as being the seat of the most important pottery of the district, and he also speaks of the manufacture of tobacco-pipes at Newcastle-under-Lyne. He gives a minutely exact description of four varieties of white and red clays, all of them found within half a mile of Burslem, the best being dug up nearest the coal, which were of close texture and would work well on the wheel; and three other clays of looser and more friable natures, called *slips*, which were usually used for painting the wares. Until 1680 a lead glazing was employed; glazing by means of salt is stated to have been accidentally discovered in that year, and first used by a potter named PALMER. About 1605 white and brown stonewares were made by THOMAS MILES of Skelton. These wares, when salt-glazed, were called *crouch-wares* by the Burslem manufacturers, who first produced them in 1690. In 1700 Burslem contained twenty-two ovens, each having eight mouths at equal distances. If the mottled jugs mounted in silver of the time of Elizabeth be really of English make, we must put back the introduction of salt-glazing by a century at least.

The first attempts that were made to imitate some Japan ware by the Staffordshire potters were not successful; but about 1690 the brothers JOHN PHILIP and DAVID ELERS, who had come over with the Prince of Orange in 1688, discovered a bed of fine clay suitable for the production of a hard compact red ware of most excellent quality. This ochreous clay was dug at Bradwell Wood, about two miles from Burslem, and by careful grinding and purification enabled these foreign potters to turn out tea-pots, coffee-pots, piggins, flower-pots, of a character quite equal, if not superior, to the Japanese red ware which had suggested their production. JOHN PHILIP ELERS appears to have been the more active of the brothers, and to have remained in Staffordshire until 1710. ELERS' ware is variously marked by an impressed square of imitative Japanese characters, often found on the pieces now extant. Agate ware, tortoiseshell ware, and fine white stoneware, were also made by ELERS. The use of calcined and pounded flint as an ingredient in Staffordshire pottery is generally attributed to ASTBURY in the year 1720: it was probably due to ELERS, but it did not come into general use until that year, from which date great and highly important improvements in the Staffordshire wares were made. The new material was used in combination with pipeclay and sand, and coloured with oxide of copper and manganese. About this time moulds of plaster of Paris were introduced from France into England by RALPH DANIEL of Cobridge, and generally adopted by the English potters. The fine salt-glazed ware of a creamy-white, the agate and tortoiseshell wares, some of the specimens being moulded in relief and enriched with oil-gilding, were thus produced. The wares produced from these moulds were distinguished only by their different shades of colour, and were known as drab, or cream-coloured, and white. Printed and painted wares also soon followed the plain varieties.

JOSIAH WEDGWOOD was born in 1730. He was removed from school at the early age of nine, and placed as a thrower in the Church-yard Pottery of his brother Thomas at Burslem. In 1744 he was apprenticed to his brother for five years, and afterwards entered into partnership with HARRISON of Cliff Bank Pottery. Before long he associated himself with WHIELDON, of Fenton, who became well known for his tortoiseshell and other richly glazed wares. In 1759 he commenced working on his own account, and it was not long before the improvements which he effected in the ordinary white ware attracted attention. He gave to this white ware delicate creamy, straw, or primrose tints, and was allowed to call it *Queen's ware*, after Queen Charlotte, by whom some specimens had been ordered. This renowned

ware was composed of the whitest clays of Dorset and Devon, mixed with ground flint, and covered with a sound vitrified glaze. It was thin and uniform in substance, thoroughly well potted, and would stand heat and ordinary acids.

His success having now become established, WEDGWOOD applied himself with the most devoted assiduity to the introduction of various improvements in the composition, glaze, and colour of his productions. He consulted the best chemists; he worked assiduously at his own experiments; and he sought the aid and co-operation of the ablest workmen and the most accomplished artists, including the great sculptor FLAXMAN. WEDGWOOD for some time had no show-rooms in London; but he subsequently secured premises for the display and sale of his useful and ornamental wares in Newport Street, and then in Greek Street. For some years the London establishment was managed by his friend and partner, THOMAS BENTLEY, a man of good address and excellent taste, but not descended, as has been affirmed, from the celebrated critic. BENTLEY was a merchant of Liverpool, and his knowledge of business was of great service to WEDGWOOD. He also secured influential patrons for the finer products of the works, and was perpetually borrowing antique sculptures, cameos, intaglios, gems, impressions, drawings, engravings, vases, seals, &c., as well as securing the services of modellers, enamellers, and designers. Having obtained the loan of valuable specimens or casts in plaster and wax, WEDGWOOD produced the most admirable copies in black basalt ware, in a fine white terra-cotta, in a bamboo or cane coloured ware, and in other improved bodies.

WEDGWOOD'S jasper pottery was produced from a white body of extraordinary delicacy and beauty, which, unlike any other ceramic composition known either in ancient or modern times, possesses the property of receiving through its whole substance, from the admixture of metallic oxides, the same colours that those oxides communicate to glass or enamel in fusion. WEDGWOOD was thus enabled to produce, in bas-relief, any figures or objects that he might desire of the purest white upon coloured grounds. The blue jasper of his grounds he obtained by adding to the mixture of his vitrescent materials oxide of cobalt, the quantity being increased as a greater depth of colour was desired. In the case of green jasper, the admixture was made with oxide of chromium. Another important discovery made by WEDGWOOD was that of painting on vases and other objects, without the glossy appearance of ordinary paintings on earthenwares. His cameos and other works are still held in high honour abroad, and at home Wedgwood ware of every description now finds ready purchasers at prices which significantly indicate its present reputation. But Wedgwood ware fell for a time into oblivion and neglect, and it must be said that for fifty years or more after his death the magnificent cameo friezes and medallions which he made for mantelpieces, as well as the smaller gems set in articles of personal use and adornment, were forgotten or lightly esteemed. Many proofs of this statement might be adduced: we here select a few prices realized at the auction sale at CHRISTIE'S of WEDGWOOD'S cameos after the death of his partner BENTLEY. The sale took place in 1781, and we find that cabinets of thirty-six large coloured medallions sold at prices varying from three to nine guineas, although the warehouse prices for them ranged between £15 and £25. At the same sale white cameos on black grounds were sold at about 2*s.* or 3*s.* apiece; they would now realize as many pounds. Indeed, during the last twenty years or so, it has been difficult for collectors to obtain genuine pieces of old Wedgwood jasper ware, even at prices several times as great as those originally charged. The manufacture is still continued, but the modern productions of Etruria lack that compactness and fineness of body, and that careful finish, which characterized the work turned out in WEDGWOOD'S life-time, or up to the end of the last century. Still it is satisfactory to know that WEDGWOOD'S discoveries, improvements, and good taste exercised an immediate and a lasting effect upon the make and style of English pottery.

At Lambeth the manufacture of stoneware has lately attained a great success. Messrs. DOULTON have always made considerable quantities of coarse stoneware glazed with salt; but during the last few years they have turned their attention to the manufacture of ornamental goods in the same class of ware, but of finer quality. SPARKES, the head master of the Kensington and Lambeth Schools of Art, has aided greatly in the artistic development of these finer salt-glazed wares, and many of his pupils are now daily engaged in turning out vases, jugs, salt-cellars, and even architectural pieces of very high merit, both in material, in design, and in colour. The ware resembles at once the old Staffordshire salt-glazed ware, and the foreign *grès cerame* or Flanders ware, of which we have before spoken. The simplest style in vogue bears ornaments of foliage or animals lightly incised on the body before firing, and filled in with a blue or brown pigment. The body is usually brown or buff when burnt, and is made of various mixtures of clays from Staffordshire, Dorsetshire, &c., with ground flint and sand: sometimes a wash of fine white clay is given to the body; sometimes the whole body is made of the finer clays which will burn white. The glazing is done with salt thrown into the kiln, as described further on; and coal is used as the fuel. This use of coal has entailed great difficulties in the attempts made to obtain an extensive range of colours which would stand the great heat of these stoneware kilns where no saggers are used, and where the impurities of the coal destroy the more delicate metallic pigments. RIX, the manager of this department, has, however, succeeded in obtaining a greater variety of tints than were ever secured by the German potters of the seventeenth century. The more lightly decorated pieces of the Lambeth pottery are not only beautifully coloured, but they are further enriched with applied and embossed ornaments in relief. Some of the best of these pieces are the work of GEORGE TINWORTH,

whose work is of very original character. His terra-cotta and stoneware, alto reliefs of scriptural subjects, are full of spirit and executed with remarkable freedom of touch. The outlined animal forms before alluded to are mainly the work of Miss Barlow, another artist employed by Messrs. Doulton. There can be no doubt that the fine works in this intensely hard and perfect stoneware, now being turned out by Messrs. Doulton, justify the high appreciation in which they are held by men of taste. We ought to add that the Lambeth Pottery also produces very admirable painted tiles for wall decoration, in an earthenware body like that of Majolica. The materials are pipe-clay from Dorsetshire, pulverized Staffordshire flint, and sand; a salt glaze is used, which renders the ware perfectly impermeable to water, and even to acids.

The Liverpool manufactories produced many fictile works of considerable interest and importance. They were started about 1670. A century later, Sadler and Green introduced the art of printing upon pottery. In 1752 Richard Chaffers made a fine white earthenware at Liverpool, and manufactured a porcelain of great excellence.

Of late years the production of *inlaid tiles* and *moulded architectural terra-cotta* has been revived, and these are now made by Herbert Minton and others. Messrs. Maw are more particularly distinguished for their tiles having geometrical designs, after the manner of the ancient tessellated pavements, and for their reproductions of Majolica. There are many other manufacturers, both of tessellated and inlaid tiles. Some of these potters have caught with great success the spirit and style of the mediæval work which is seen in the splendid tiles of Malvern Abbey Church, of the Chertsey tiles, and of many similar relics of the skill and artistic feeling of our potters in the middle ages.

Some of the best terra-cotta, in creamy white, in buff and light red, is made by the Watcombe Co., near Torquay, Devon. The statuettes in this fine unglazed body are often very pleasing in style, while the quality of the ware is marked by a singular smoothness and delicacy. The decorations are, both in enamel colours and in applied cameo reliefs, of a different tint to the ground. The clay chiefly used at Watcombe is of post-tertiary age. It contains 57·8 per cent. of silica; 20·6, alumina; 7·8, ferric oxide; 1·7, lime; 3·9, potash; 1, magnesia; and about 7 per cent. of water, with a trace of organic matter.

Porcelain.—Although vases and other pieces of Chinese porcelain had found their way into Europe before the Portuguese doubled the Cape of Good Hope in 1497, it was not until after that event that this porcelain became well known to the various European nations. The earliest known mention of china in England is in 1506. In 1600 the English East India Company was founded; and having at length formed an establishment at Gambron, in the Persian Gulf, it was enabled to introduce Chinese porcelain directly from that port into England, and hence it became known as Gambron ware. However, according to some writers, Gambron ware was a fine sort of Persian *faience*. In 1631 china was commonly imported into this country.

The cause of the translucence that characterized the porcelain of the East remained undiscovered until 1709, when Böttcher first succeeded in producing, at *Meissen*, the true porcelain known as *Dresden China*.

The two chief components of porcelain are entitled *kaolin* and *petuntse*. The kaolin is an infusible substance, consisting of clay, derived from decomposed felspar; and the petuntse or white paste, which is fusible, and produces the translucent quality of the ware, is composed of felspar and quartz—that is, silica—reduced to powder. The two classes or varieties of porcelain, severally distinguished as *hard paste* and *soft paste*, contain the two principal ingredients in different proportions. The hard contains a greater quantity of kaolin, and therefore more alumina and less of silica; in the soft the proportion of silica and felspar is increased. The former acquires a greater and the latter a less density. The latter also is soft in two senses: first, as being less able to resist a very high temperature; and secondly, since the paste, where unprotected by the glaze, is easily scratched by an iron instrument. It must be added, that besides the naturally soft paste—*pâte tendre naturelle*—there is a porcelain formed from a paste that is artificially soft—*tendre artificielle*.

Böttcher used the kaolin of Aue, in the Erzgebirge, and the most profound secrecy was rigidly enforced with respect to the entire process of the manufacture. Notwithstanding every precaution, however, certain workmen escaped from Meissen; and the secret having thus become in some degree divulged, other porcelain manufacturers arose, one by one, in various parts of Germany. In the year 1720 and 1751 the great establishments of Vienna and Berlin were severally founded.

In 1713 Reaumur commenced a series of experiments which paved the way for the use of kaolin in the Sèvres manufactory. True kaolin was accidentally discovered in 1768 at St. Yrieix, near Limoges; and having been ascertained by Macquer to be both abundant and of good quality, it was introduced at Sèvres, where in 1769 the production of hard porcelain was regularly established. It is very remarkable that the quarries of St. Yrieix produce not only the kaolin, but also the pure white felspar or petuntse, which is indispensable in the production of porcelain.

The peculiar ground colours of the Sèvres porcelain are distinguished as *blue-de-roi*, a rich, deep blue; *bleu-turquoise*, a pale blue, the tint of the jewel; yellow, or *jonquille*, a full, glowing green, or *vert-pré;* and the lovely rose colour, called after Madame Dubarry, *rose-Dubarry*.

Some degree of uncertainty hangs over the date of the first English porcelain manufactories at Bow and Chelsea, nor is it distinctly known what were the clays employed in the earlier works at Derby and Worcester. The natural kaolin of Bovey Tracey, Devon, is said to have been worked in 1730; but the kaolin of Cornwall, which caused

such great and important improvements in the porcelain manufactures of England, was not discovered by COOKWORTHY until about 1755. Kaolin, or *china-clay*, is now chiefly prepared from the granitic rocks of both Devon and Cornwall; and, as in the instance of St. Yrieix, petuntse, called also *china-stone*, is obtained from the same Cornish rocks which also furnish the kaolin. Bone is an ingredient in common use in the composition of English porcelain.

When the Bow works were given up in 1775, the moulds and models were removed to Derby, where the porcelain became celebrated. The Derby china is very translucent and of fine quality.

It is very probable that bone earth, that is, the ash of burnt bones, was first used in porcelain made at Bow about 1749, though the application of this material has been attributed to PENNINGTON of Liverpool, in 1760, and to SPODE, in 1800. Our authority for this idea is the patent taken out by FRYE of the Bow works, in 1749, where he speaks in guarded terms of a certain virgin earth produced by calcining animals, vegetables, and fossils, mixed with flint or sand and some pipe-clay, as the materials of his porcelain. The evidence afforded by analysis is, however, conclusive on this point. Numerous fragments of unglazed early Bow porcelain have been recently exhumed on the site of the works; on careful analysis they were found to contain over 17 per cent. of phosphoric anhydride (P_2O_5), corresponding to nearly 30 per cent. of phosphate of lime.

All the different English factories which we have named above produced a kind of porcelain very different from the true Oriental sort. It was soft and easily injured, both by heat and corrosive liquids. But true porcelain of the hardest character and excellent quality has been made in England, first of all at Plymouth, by WILLIAM COOKWORTHY, who patented his invention in 1768, and afterwards at Bristol, by RICHARD CHAMPION, who purchased COOKWORTHY'S rights, and improved the methods of making and decorating the ware which he had devised. The discovery of the true kaolin or china-clay in Cornwall, by COOKWORTHY, about the year 1755, was the origin of these works at Plymouth and Bristol. As the large deposits of this mineral in Cornwall are of the finest quality, and are, moreover, associated with abundant supplies of felspar suitable for glazing the ware, and of china-stone, which is required for admixture with kaolin in the body or paste of the hard porcelain, it is not surprising to find that the old Bristol porcelain of CHAMPION (made down to the year 1781) is almost identical with that of China. An analysis by CHURCH, of the handle of a tea cup authenticated as made by CHAMPION, gave the following results:—

	Per Cent.
Silica,	62·92
Alumina,	33·16
Lime,	1·28
Alkalies,	2·64

Thus it will be seen that the alkalies and lime of this porcelain do not amount in all to 4 per cent., while the average amount in fine Oriental porcelain appears to be 6; in Dresden, 6·3; and in hard Sèvres, 7 per cent.

There is a curious and obscure make of hard porcelain to which we may here appropriately allude. It would appear that a certain Count BRANCAS-LAURAGUAIS not only made hard porcelain at an early date in France, but that he worked out the same subject in England. His wares, marked usually with an L and B interlaced, are excessively rare (three out of the ten known specimens having been, moreover, destroyed in the Alexandra Palace fire in 1873), but they are undoubtedly of the very hardest paste. One piece, no longer extant, was almost certainly decorated at Chelsea, and it has been conjectured that it was made there from Cornish materials. The evidence for this is partly internal, partly derived from a letter by Dr. ERASMUS DARWIN to WEDGWOOD, in which he speaks of the Count's statement concerning the abundance of the proper materials for hard porcelain to be found in England. We ought to add that a kind of hard porcelain, containing more soda than other sorts, was made by Dr. DWIGHT of Fulham towards the close of the seventeenth century.

In 1751 the manufacture of porcelain was introduced by Dr. WALL at Worcester. The earliest efforts were directed to the imitation of the porcelain of China and Japan. About 1756 the important process of *transfer printing* was discovered or adopted. Steatite from Cornwall is believed to have formed a considerable ingredient in the paste of the Worcester porcelain body, as made during the eighteenth century. Bone-ash was also frequently used, as the analysis of authentic specimens shows. The present productions of the Worcester works comprise the most exquisite works of ceramic art, together with every variety of useful objects. Nearly contemporaneously with the works at Worcester are those that still flourish on the right bank of the Severn, at Coalport and Colebrook Dale, and other places in the same neighbourhood in Shropshire, and produce vast quantities of excellent porcelain.

PROPERTIES OF CLAY.—Clay consists of hydrated silicates of aluminium, in combination more or less with other substances derived from the felspathic rocks, which by their disintegration and decomposition have formed the clay; the silicates of potassium and sodium, which form constituents of the felspar, having been dissolved out by water during the decay of the rocks. The chemical formula of the more important varieties of clay may be represented by Al_2O_3, $2SiO_2$, $2H_2O$; but the analyses of different clays from different places give somewhat variable proportions of the Al_2O_3, the SiO_2, and the water. Besides these variations, most clays are further intermingled with substances foreign to them in their original localities, fragments of undecomposed rock, carbonate of lime, magnesia, and the oxides of iron, certain proportions of potash, and variable amounts of silica in the hydrated condition—all of which modify the character of the clay and its

applications, according as one or other of these ingredients predominates.

Pure clay is soft, more or less unctuous to the touch, white and opaque, and when breathed upon emits a characteristic odour; it may be converted by water into a doughy, tenacious, plastic paste, insoluble in water. When slowly dried and exposed to a high temperature clay shrinks considerably, and splits into masses extremely hard, and does not undergo fusion in the most powerful blast furnace; the stronger the heat to which it is exposed the more dense, sonorous, and hard does it become, although still porous enough to absorb water with avidity. Pure clay dissolves in borax at a high temperature, producing a transparent glass; with carbonate of soda it forms a green glass; if ignited with solution of cobalt it assumes a blue colour. Clay is insoluble either in nitric acid or dilute hydrochloric acid; but boiled with diluted sulphuric acid until the acid begins to evaporate, the alumina is dissolved out, together with a small quantity of silica. By boiling in a solution of carbonate of soda, the quartz, sand, felspar, &c., may be separated. The presence of clay in any soil may be readily distinguished by the absorbent quality which it exhibits; when applied to the tongue or lips in a dry state, it adheres to them strongly, absorbing the saliva from their surface. It is this absorbent property in clay which causes it to retain ammonia in the soil. The ingredients which most diminish the plasticity of clay are sand, iron, lime, and magnesia. Clays which contain an excess of iron or lime fuse to a rough glass; this can be corrected by the addition of silica to a large quantity of these ingredients. The fixed or *fireproof* clays are thus distinguished from the *fusible* ones. Those containing iron are either red, yellow, or blue, after firing, according to the quantity of the metallic oxide they contain, and the degree of heat to which they have been subjected. Many kinds of clay are permeated by an organic substance, or by finely divided iron pyrites, which gives them a blue, bluish-grey, or black colour. When this colour arises from organic matter it is discharged in firing, but when from pyrites a yellow or pink colour is often produced on heating.

It is upon the property which clay possesses of being converted by heat into a firm compact mass, no longer influenced by the action of water, that its employment in the preparation of bricks and vessels of various kinds depends; and with a view to this object the different varieties of clay have been classified into *fireproof*, *fusible*, *calcareous*, and *ferruginous*—the calcareous being those which contain a large proportion of earthy carbonates, particularly lime, while the ochry or ferruginous clays contain much oxide of iron, and possess a red-brown colour.

Fireproof Clays.—*Kaolin* or *Porcelain earth* is one of the most important materials in the production of porcelain. It is an earthy, pure white, greyish, or milk-white substance, easily pulverized. It occurs in granitic rocks rich in felspar, but containing little mica or hornblende, &c. The chief localities of this substance are Seidlitz, near Meissen; Morl, near Halle; Obernzell and Diendorff, near Passau; St. Yrieix, near Limoges, Department Nièvre; St. Austell in Cornwall; China and Japan. Kaolin burns perfectly white. The subjoined analyses exhibit its composition:—

	Kaolin from				
	St. Yrieix. (Berthier.)	Aue. (Kuhn.)	Passau. (Fuchs.)	Halle. (Bley.)	St. Tropez.
Silica,	47·09	47·64	43·65	39·62	55·80
Alumina,	36·41	35·97	35·93	45·00	26·00
Potash,	1·56	—	—	—	8·20
Magnesia,	2·94	—	—	3·32	0·50
Lime,	—	1·57	0·88	0·07	—
Ferric oxide,	—	—	1·00	—	1·80
Dioxide of manganese,	—	—	—	0·19	—
Water,	12·00	13·18	18·50	10·00	7·20
Loss,	—	1·64	0·04	1·80	0·50
	100·00	100·00	100·00	100·00	100·00

Cornish-stone consists chiefly of quartz and felspar, mica not being entirely absent. This rock, sometimes called pegmatite, after exposure to the decomposing action of the weather for some time becomes easily pulverizable. It consists of kaolin, undecomposed felspar, and quartz.

Dr. Lyon Playfair has made the following analyses of two specimens of kaolin from Bluebarrow and from St. Stephens, Cornwall:—

	Bluebarrow.	St. Stephen.
Silica,	45·52	46·38
Alumina, with trace of oxide of iron,	40·76	38·60
Lime,	2·17	3·47
Potash, with trace of soda	1·90	1·77
Magnesia, phosphoric acid, and sulphuric acid,	traces.	traces.
Water, with a small quantity of organic matter,	9·61	9·08

The China Clay Works at St. Stephens, Cornwall, are composed of extensive tracts of felspathic rock in a high state of decomposition, 20 feet thick, standing on a declivity. But in some cases, as in the famous mine of Carclaze, near St. Austell, the clay extends to 120 feet in depth from the surface. Trenches are formed around spaces of the rock, and strong currents of water directed into them, which carry off the decomposed portion, united with small micaceous particles. These streams are directed into large pits, termed *mica pits*, where the particles are deposited. The pits are fitted with boards, which are raised from time to time as required; and as the mica rises in the pit, the finer particles of clay being held in suspension flow over the boards, and are conveyed by channels into tanks of very large dimensions. When these large reservoirs are filled, the washing process is stopped, and the fine clay is allowed to settle, and is removed in the state of slip or thin paste to more shallow drying tanks, surrounding the general reservoir. The latter are about 18 inches deep, and in these the slip is allowed to remain until it becomes a stiff paste. Cutting tools are then passed through

crosswise, and the superfluous water run off. The mass is afterwards cut into squares, which are placed to dry on a space previously sanded or clayed to prevent the squares of clay being mixed with extraneous matter. The squares are arranged in the most convenient manner for drying, and dry clay is sifted over them. When in a sufficiently hard state, women are employed with sharp triangular scrapers, to remove all the surface clay or sand with care, and the squares are then ready for shipment. The scrapings are collected, and again passed through the washing process, so that little or no loss of materials can arise. Artificial heat is now largely used in drying the blocks of Cornish china clay.

Granite or Cornish-stone clay, previously dried at 212° Fahr., or 100° C., was found to consist of—

	1.	2.	3.
Silica,	46·32	46·29	35·65
Alumina,	39·74	40·09	32·50
Monoxide of iron,	·27	·27	1·65
Lime,	·36	·50	traces
Magnesia,	·44	—	
Water and some alkali,	12·67	12·67	30·05
Loss,	0·20	0·18	0·15
	100·00	100·00	100·00

Specimen No. 3 was analysed by Richardson in its undried state.

Another kind of clay, nearly allied to kaolin, and which occurs in large quantities at Houscha, near Bayonne, and is often used in the manufacture of porcelain, has been found by Berthier to be halloysite, mixed with a product of the decomposition of pegmatite. It forms a connected, tolerably soft, and easily pulverizable mass, is of a dull white colour, and opaque; it affords no dough when kneaded with water, and is consequently not plastic. Berthier found it on analysis to be represented approximately by the formula:—

$$2Al_2O_3 + 3SiO_2 + 8H_2O.$$

Pipe-clay is of different colours, very tough, exceedingly plastic, and becomes white, or sometimes yellow, in the fire, from the presence of a small quantity of iron. It is used in the manufacture of stoneware, clay pipes, earthenware, &c., and occurs in very considerable quantities. The most generally known localities are on the Lower Rhine; at Cologne and Coblentz, near Halle; in Devonshire and at Stourbridge in England; and at Dreux and Forges-les-Eaux in France. The following analyses show that these clays contain but little iron and foreign earths:—

	Grossalmerode. Forchhammer.	Strasburg. Berthier.	Stourbridge. Berthier.	Stourbridge. Muspratt.	Forges-les-Eaux. Berthier.	Coteau de Prairie, N. America. Catlin.
Silica,	15·906	66·7	63·7	62·99	52·0	48·2
Alumina,	11·170	18·2	20·7	20·04	27·0	28·2
Lime,	3·504	—	—	0·30	—	2·6
Magnesia,		0·6	—	0·94	—	6·0
Potash,	0·786	—	—	—	—	—
Water,	4·119	12·0	10·0	10·70	19·0	—
Ferric oxide,	—	1·6	4·5	trace	2·0	5·0
Manganese dioxide,	—	—	—	—	—	0·6
Residue,	64·030	—	—	—	—	—
Loss, &c.,	0·485	0·9	1·1	5·03	—	10·0
	100·000	100·0	100·0	100·00	100·0	100·0

Potter's Clay.—Among the *fusible clays* may be classed *Potter's clay*, generally used for the production of the commoner kinds of clay-ware. It is distinguished from pipe-clay by the presence of a very sensible quantity of iron and some lime, is more easily disseminated through water, and has the same amount of plasticity as pipe-clay. In colour it is generally red, or brown-red, and contains a considerable amount of organic remains, fragments of stone, and iron pyrites. The presence of ferric oxide causes it always to assume a red or yellow hue after burning; and according to the quantities of this ingredient and of lime which it contains, it fuses more or less easily into a dark, vitreous mass or slag.

The common potter's clays in England are found in layers or strata lying over each other, each stratum possessing some distinctive property which fits it for a peculiar purpose. That which is called the sandy stiff, or ball-clay, is the upper layer, and from the considerable quantity of silica it contains is used for making salt-glazed ware. On analysis this clay, dried at 100° C., will be found to yield:—

Silica,	66·68
Alumina,	26·08
Ferrous oxide,	1·26
Lime,	·84
Magnesia,	trace.
Water,	5·14
	100·00
Its specific gravity,	2·558

Blue Clay, also one of the fusible clays, is considered the best layer of clay in the whole series. In colour it is greyish, but burns perfectly white, approaching china-clay in character. When dried at 100° C. its analysis shows the following composition:—

Silica,	46·38
Alumina,	38·04
Ferrous oxide,	1·04
Lime,	1·20
Magnesia,	trace.
Water,	13·44
	100·00

This clay is also called Dorsetshire and Poole clay, Poole being the port of shipment. It is obtained

chiefly from the neighbourhood of Wareham, and large quantities are shipped annually for Staffordshire and other parts of the United Kingdom.

These mines of clay extend upwards of seven miles from the port of shipment. The superincumbent strata of soil, sand, and bituminous matter vary from 60 to 80 feet in thickness, the clay lying beneath a fine bed of sand. The heading of the clay is mixed with sand, and formerly was thrown aside as worthless; but of late years this has been extensively used for fire and fancy bricks, and for other ornamental and useful purposes. The bed of clay, once fairly laid open, is worked by cutting out cubical blocks weighing 30 to 40 lbs.; and to facilitate the operation, currents of water are directed into small dams, into which the workmen constantly dip their spades. The beds vary from 3 to 6 feet in thickness. In the vicinity of Glasgow is a surface clay containing much ferric oxide. It is in great demand for common black ware, flower-pots, and red bricks, articles which do not require to be exposed to any very high temperature which would fuse them.

Fire-clay.—This variety of clay is very abundant. From the porosity of its substance, it is well adapted to resist high temperatures. Its principal use in the potteries is for making saggers, or vessels for protecting the ware from the flames during firing. Fire-bricks, crucibles, and melting-pots for glass-works are made from this clay. Analyzed, it gives the following percentages:—

Silica,	66·16
Alumina,	22·54
Ferrous oxide,	5·31
Lime,	1·42
Magnesia,	trace.
Water,	3·14
Loss,	1·43
	100·00

Calcareous Clays.—*The Marls*, a term which applies to all those deposits containing clay and carbonate of lime, the latter in considerable quantity. These mixtures are mechanical. Those in which lime preponderates are named *Calcareous Marls;* those in which alumina is most abundant, *Aluminous Marls.* Aluminous marls are used in the manufacture of several kinds of pottery. The proportion of their constituents will be seen from the following analyses:—

Locality.	Silica.	Alumina.	Ferrous Oxide.	Carbonate of Lime.	Carbonate of Magnesia.	Alkali.	Analysts.
Abydos,	52·00	16·17	6·15	13·97	trace.	trace.	Salvetat.
Bonnefonds,	40·00	13·21	2·04	34·12	0·15	—	"
Belleville,	46·03	17·28	5·70	27·64	—	—	Buisson.
Chambray	49·50	29·00	3·00	18·00	0·50	trace.	Laurent.
Savone,	37·00	11·00	6·50	55·00	—	—	Buisson.
Viroflay,	39·00	18·00	1·00	40·00	trace.	—	Lecoq.
Villom,	30·00	20·00	2·00	46·00	—	—	"

A small portion of the lime in the marl is generally in combination with silica.

Loam is the commonest and the least pure variety of clay belonging to the more recent alluvial formations; it is less uniform than any of the foregoing varieties—sand, gravel, stones, wood, roots, and all kinds of vegetable remains, being mixed up with it in large proportions. It is soft and easily reduced to powder, absorbs water with avidity, and forms with it a soft paste, which is much less plastic and fat than that obtained from pipe or potter's clay. As it occurs almost everywhere, it is the universal material for making bricks.

Flint, *Quartz*, *Silica*, or *Silicic Acid* (SiO_2), is found abundantly as flint, an amorphous, black or brown coloured mass, which occurs with chalk in roundish or irregularly shaped nodules, weighing from a few ozs. to several lbs.; it contains moisture, an organic substance, and occasionally iron. Whatever its original hue may be, it always burns white, and acts the part of a bleaching material, neutralizing imperceptibly the yellow or greyish colour of the clay. In preparation for use, the flints are calcined in upright furnaces, constructed similarly to ordinary lime-kilns. The flint is thus rendered white and disintegrated, splits in all directions, and is sufficiently brittle and soft to admit of being crushed in the stamping mill, and ground under water in the block mill.

Porcelain.—*Tender Porcelain.*—This appellation has reference to the feeble resistance offered by this class of wares to the high temperature of the kiln, and the softness of the body and glaze compared with true porcelain. It may be classed under two heads:—"Natural," or the tender porcelain of England, in which kaolin or china-clay is the basis, though associated with bone earth and sometimes with steatite; and "Artificial," or the tender porcelain of France, in which the mass is a mixture of different substances, consisting mainly of silica with alkaline and earthy salts.

English Tender Porcelain.—So named because the manufacture is exclusively confined to this country, local reasons being unfavourable to the production of true porcelain. The chief of these is the want of a cheap material for the construction of the saggers able to stand the firing, the present loss of saggers in Staffordshire being estimated at from 8 to 10 per cent. at each firing.

The crude materials which enter into the composition of ironstone china are *plastic clay*, *kaolin* or *china-clay*, and *granite* or *Cornish-stone*, with bone earth, *chalk flints*, and occasionally *steatite* or *soapstone*. A pure specimen of Cornish steatite, recently analyzed by Church, gave the following percentages:—

Magnesia,	32·89
Silica,	63·18
Water,	4·47
	100·54

Usually traces of alumina, manganese, iron, lime, and alkalies are also present.

The introduction of steatite is said to diminish the contraction of the wares in the furnace. The bone earth contains phosphate of lime, carbonate of lime, and a little magnesia and fluoride of calcium in the form of a perfectly white substance. The phosphoric acid diffuses itself at a high temperature through all the materials, uniting them into a translucent enamel, which, being less apt to shrink and lose its form than the hard China body, may be baked in larger kilns, and with less risk of loss to the manufacturer. All these ingredients are ground, suspended in water, and boiled down into a paste. A frit is then prepared, of which the mass is made up with other substances, as follows:—

FRIT.		MASS.	
Bone,	100	Burnt bone,	600
Sand,	90	Kaolin,	300
Pear-lash,	7	Cornish-stone,	360
		Frit,	40

Or the mass is not fritted in part, but, as in the case of table-ware, mixed all at once in the following proportions:—Bone, 450; Cornish-stone, 200; china-clay, 160; plastic blue clay, 45.

Other mixtures for English china-ware are:—1. Bone, 46; china-clay, 23; Cornish-stone, 31. 2. Bone, 36; Cornish-stone, 21; Cornish-clay, 21; flint, 12. 3. China-clay, 600; felspar, 335; bone, 840. 4. Bone, 320; china-clay, 225; Cornish-stone, 230. The bone and flint are sometimes fritted to produce the highest degree of vitrescence, and then mixed up with other ingredients. A little Dorset clay is frequently added for large pieces, to give more ductility in working and greater stability in the fire. In all cases the ware, from the large proportion of clay in the mass and its extreme plasticity, requires to be fired twice. The first firing lasts longest, being of from forty-eight to fifty hours' duration; and the temperature is gradually raised during the whole time, the heat of the kiln ranging, according to the composition of the ware, from 100° to 110° Wedgwood's pyrometer. It is somewhat singular that this instrument is never used in the potteries, the proper temperature being regulated by small trial pieces of the same material as the goods to be fired. When the trial pieces show that the heat is sufficiently raised, the firing is discontinued, the fire and ashpit doors closed, and the whole left to cool during twenty-four or thirty hours. The glaze is then applied to the ware, and the articles undergo a second firing, but neither at so high a temperature nor of so long duration.

Glazes.—Those most commonly used are flint, quartz, sand, felspar, gypsum, carbonate of lime, borax, boracic acid, chloride of sodium, potash, soda, and oxide of lead. Some glazes are first formed into *frits*, imperfectly vitrified bodies so termed, and afterwards pounded for use.

Coloured glazes are made with the addition of nearly pure oxides of manganese, copper, iron, chromium, cobalt, &c.; *opaque glazes* or enamels, by the addition of oxide of tin or phosphate of lime; for which see *Porcelain*, *True*, and *Earthenware*. Some of the ordinary lead glazes for soft porcelain are given below:—

I.

Felspar,	38
Lynn sand,	24
Carbonate of lime,	11
Borax,	27

fritted together and mixed as follows:—

Frit,	60
Cornish-stone,	20
White lead,	20

II.

Cornish-stone,	52
Flint,	38
China-clay,	30
Carbonate of lime,	45
Borax,	90

fritted together and mixed as follows:—

Frit,	320
Cornish-stone,	50
Flint,	50
White lead,	60

III.

Cornish-stone,	60
Felspar,	60
Flint,	75
Carbonate of lime,	40
Borax,	100

fritted together and mixed as follows:—

Frit,	250
Cornish-stone,	65
White lead,	65

The temperature of the glaze kiln ranges about 60° Wedgwood, but is varied according to the circumstances of the manufacture. The time required for firing the glaze kiln averages about seventeen hours, the consumption of coal being nearly 6 tons.

The Artificial Tender Porcelain of France presented the following characteristics:—*Body* fine, dense, texture almost vitreous, hard, translucid, fusible at a high temperature; *glaze* vitreous, transparent, containing lead, and tolerably hard. The manufacture of this class of ware was carried on at Sèvres between the years 1750–1804. During this period it obtained great celebrity, and from the circumstance of the manufacture being now no longer continued, having given place to the improved method of Böttcher, the following composition is now interesting as a matter of curiosity:—

Melted saltpetre,	110
Sea-salt grey,	36
Alum, generally burnt,	18
Alicante soda	18
Gypsum from Montmartre,	18
Sand from Fontainebleau,	300
	500

Porcelain or *True China* is the finest description of ware. It is made from *kaolin*, or china-clay, and a *flux*, composed of felspar, with the addition of quartz, chalk, and gypsum, which, softening and becoming vitrified in the heat of the porcelain kiln, forms a kind of cement, binding the clay firmly together, and producing a dense, impenetrable, translucent mass, of a uniform texture throughout, and imper-

vious to liquids. The transparency of porcelain arises, therefore, from the clay body becoming saturated with a mass of glassy flux. Under the microscope the two ingredients can be clearly distinguished from each other, the milky mass appearing as a transparent ground, mixed with an opaque substance composed of minute globules, arranged in a lineal direction, one on the other, as articulated threads or little rods, which are interwoven and cross each other in all directions; the want of absolute transparency in the mass being due to the reflection and refraction of light from the surface of these crystals.

The Glaze is composed of *felspar*, sometimes mixed with a little gypsum, but with an entire absence of lead or tin. The absence of lead causes the glaze to be very hard, and to resist scratching. The mass for porcelain vessels is composed as follows:—

FINE OR HARD PORCELAIN—COMPOSITION OF THE MASS.

In Berlin.

For Domestic Uses, Plates, Dishes, &c.		For Ornamental Purposes.	
Kaolin from Morl,	76	Kaolin from Morl,	25
Felspar,	24	Kaolin from Beidersee,	50
		Felspar,	15
		Pure sand,	10

In Vienna.

Kaolin from Auerbach,	72
Felspar,	12
Quartz,	12
Gypsum,	4

In Sevres, near Paris. For Vessels.

Kaolin from St. Yrieix,	48
Sand, separated from above, containing felspar,	48
Chalk,	4

In St. Petersburg. For Tableware.

Kaolin from Risansky,	50
Felspar, Finland,	25
Quartz,	25

In Copenhagen.

Kaolin from Bornholm,	40
Quartz from Arendal,	33
Felspar,	27

In Meissen, Saxony—commonly called Dresden Porcelain.

For Domestic Purposes.		For Ornamental Purposes.	
Kaolin from Aue,	18	Kaolin from Seilitz,	37
" " Sosa,	18	Quartz,	37
" " Seilitz,	36	Lime from Pirna,	17½
Felspar,	26	Broken porcelain,	8½
Broken biscuit porcelain,	2		

In Nymphenburg, near Munich.

For Low Temperatures.		For High Temperatures.
Kaolin from Passau,	62·5	65
Quartz,	19·0	21
Sand separated by water from kaolin,	6·0	4
Gypsum,	5·0	5
Broken porcelain,	7·5	5

The following analyses of hard porcelain are given:—

	Berlin.	Chinese.	
		Superior.	Inferior.
Silica,	72·96	71·04	68·96
Alumina and Monoxide of iron,	24·78	22·46	29·24
Lime,	1·04	3·82	1·60
Alkali,	1·22	2·68	—
	100·00	100·00	99·80
Specific gravity,	2·419	2·314	2·314

Preparation of the Material.—Crude kaolin is not sufficiently pure for the purpose of manufacture, being a mixture of real kaolin with undecomposed felspar and particles of quartz, both of which must be separated or finely ground and mixed, to form a uniform substance throughout.

The kaolin is separated from stones, grit, &c., by washing in a succession of tubs provided with hair sieves. The argillaceous kaolin is carried into the last vessel, where it is allowed to deposit completely before the water is drawn off from the finely-divided clay. This process of decantation supplies a sufficient amount of felspar and quartz in the state of sand, the strong and argillaceous varieties giving each their particular kind of sand and crude kaolin. Sometimes machinery is employed for the stirring or kneading up of the mass with water.

Chalk or pure limestone is a constituent of the porcelain paste. At Nymphenburg, as in Meissen, fragments of old porcelain are also added. For the production of the best class of porcelain much depends upon the careful selection of the kaolin and material. Great care must likewise be bestowed upon the uniform incorporation of the ingredients. To insure this edgestone mills are employed.

The materials of all kinds having been ground, they are mixed together by measure in a liquid state, the proportion by weight of solid matter contained in a cubic foot of each separate specimen of *slip* having been previously ascertained, and none of the material being allowed to settle down, but each forming a thickish uniform semi-liquid mass.

The incorporation of the *mass* is effected in large cisterns or tanks under constant stirring, the paste being afterwards so far freed from water as to form a kneadable, dough-like mass. This is done by artificial heat, or by the mixture in sacks of a strong and closely-woven texture, the threads being carefully freed from filaments, so as not to attach themselves to the paste, and which previous to use have been well soaked in hot linseed oil, giving them more durability and impermeability to water. A number of these bags being placed between two boards, pressure is applied by means of a long lever, loaded upon the long arm, and having the shorter arm placed against one of the boards, so that in this way the pressure may be maintained as long as desirable. A press of this description will prepare for use about 1300 lbs. of paste in three hours.

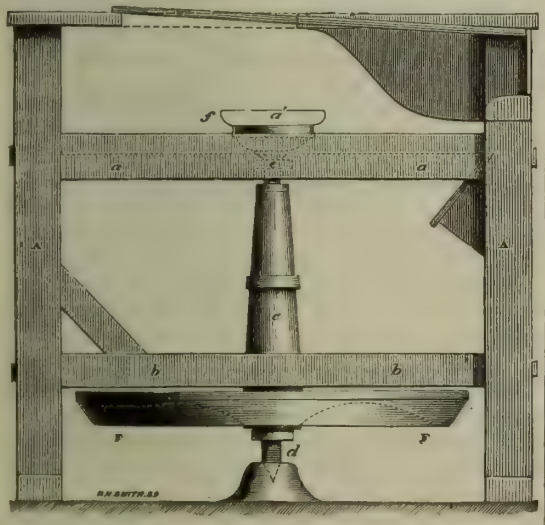
On removal from the sacks, the paste is firmer on the outside than in the interior. The defect is obviated by a process called *slapping*, the clay being forcibly thrown repeatedly against a hard stone or slab of gypsum. Sometimes treading under foot, or maceration between metallic plates with a stamper, is substituted for the slapping process.

The felspar and lime in the paste, not being plastic

ingredients, and always amounting to one-fourth or more of the whole, considerably interfere with its plasticity, rendering it very much below that of pure clay. The forming and moulding process is consequently one of great expense and difficulty, so much so, that while a workman employed with assistants in preparing plates from the more plastic earthenware, can produce 600 in ten working hours, not more than 60 or 80 plates of porcelain can be moulded in the same time. Every precaution and endeavour is therefore used to increase its plasticity —such as mixing it with fragments from the moulding operation, continued treading and kneading, and, what is found to be of greater utility, the storing it away in moist layers, in order to engender a peculiar species of fermentation. The superior value of clay that has been kept a considerable time is well known, and it is never desirable to work paste that has not been stored away in a moist state at least for a year. So fully aware are manufacturers of the efficacy of this fermentation, that attempts are sometimes made to induce it by the addition of honey, syrup, &c., to the mixture.

Forming or Moulding of Porcelain.—The goods are formed either upon the *potter's lathe* or *throwing wheel*, in *moulds* or by *casting*. The form in which the wheel is now employed in the porcelain manufacture is shown in Fig. 1.

Fig. 1.



The *thrower* seats himself upon a stool, supporting himself with one foot against the board, *b b*, so as to obtain a sufficiently stable position to enable him to rotate the wheel, F F, with the other foot. The mass of dough, as received from the *slapper*, is cut up into portions by means of a brass wire, each portion being weighed by an assistant called the *baller*. The thrower receives one of these masses, and dashes it down upon the centre of the revolving block of gypsum, *a'*. The thrower now presses both hands against the mass, which, being kept in constant rotation, gradually acquires a round form; his hands being maintained in a smooth state by dipping them into a vessel containing a quantity of water and paste held in suspension. The next operation consists in squeezing out the air. The workman then forces both his thumbs downwards into the centre of the mass, producing a cavity, which is enlarged as he removes his thumbs one from the other, producing a bell shape. The sides of the half-finished vessel are then closely pressed in a slightly upward direction between hands and thumbs, and being lessened in thickness increase correspondingly in height, according to the nature of the required vessel. It is in this manner that all vessels of a circular form in horizontal section are produced.

In this process of forming by the hand upon the lathe the inequalities of the skin produce serrated spiral lines upon the surface of the ware, destroying its neatness and cleanliness. This circumstance, in conjunction with that of the plasticity of the mass not being sufficient to admit of its being worked by hand to that degree of tenuity required by commerce, renders a further operation necessary to bring it to the proper dimensions and perfection of form—the crude shape only being obtained upon the wheel.

All vessels of an oval or angular shape which cannot be formed by turning, receive their shape by pressure in gypsum *moulds* fixed upon the wheel.

The pieces after they leave the lathe cannot be dried in a stove or current of air, or even by exposing them to the sun; for by such means they are desiccated only upon the outside, while the interior still contains a sufficient quantity of moisture to cause them to split with a kind of explosion in the furnace. They are, therefore, carefully stowed away in the shade upon wooden shelves, until no more moisture evaporates from them.

Sometimes the inner surface only of the ware is formed by the hand, the paste being pressed against the mould during its rotation, forming the vessel; the sheets of paste, considerably thicker than the sides of the future vessel, being prepared by rolling on a moistened gypsum slab under a wooden roller. When, from the elegance or complication of form, the admission of the hand into the mould is impossible, double moulds are used.

The porcelain paste, from the nature of its ingredients, is exceedingly susceptible to injuries from the least inequality of pressure in the moulding—injuries which are only made apparent at a period of the manufacture when it is too late to rectify them. The principal cause of these is the difference in shrinking during the drying and firing of the parts which have been subjected to different degrees of pressure. These defects are not so apparent when slight pressure only is applied; but when the pressure is increased and applied more unequally, they become so marked and unsightly as to render the article useless. Moulding presses are, therefore, only used for objects of small dimensions, in which perceptible differences in the consistency of the mass cannot occur; for larger vessels they are almost entirely discarded.

For the purposes of casting, the slip is stirred up

into a thick but perfectly liquid state, and passed through sieves, that all granular particles and bubbles of air may be separated, the number and nature of the moulds depending upon the form and elaboration of the article required.

The pieces must remain in the moulds for a considerable time before they acquire proper consistency; the operation of moulding, therefore, requires much time and numerous moulds. Many articles likewise, even without appendages, such as a vase with a narrow neck, cannot be cast in one circular piece, since it could not be extracted from the mould. Such articles can only be made by casting in two halves, to be afterwards joined together.

In casting, the pieces are never perfect or free from blemish as they leave the moulder, but require often tedious finishing processes, such as *turning*, *retouching*, *ornamenting*, and the adaptation of the separately moulded pieces to each other.

Many articles are made much thicker upon the throwing-wheel than they appear when finished, the superabundant mass being turned off in a lathe. In this operation the piece is fastened to the gypsum slab of the throwing-lathe by moistening the bottom, or fixed on to the lathe in a horizontal position by means of an ordinary chuck, as the case may require, ordinary sharp flat knives being used as tools in place of the chisel. One of the chief points in the finishing operation consists in the removal of the edges or seams caused by the penetration of the slip into the joints of the moulds. It is necessary that the seams should be carefully pared away with a knife, as, if removed by pressure only, they appear again after burning.

The casual cracks and indentations have at this stage of the manufacture to be carefully filled up, and all engraved or carved work, which requires cutting away with the knife, to be performed. Frequently an ornamental appearance is imparted to the ware in this state by impression upon its surface with the *roulette* or stamp, in the use of which turpentine is applied to prevent adhesion to the paste, the fatty oils not producing the necessary effect. Such parts as handles, feet, &c., are formed or moulded separately, and fixed upon the porcelain before firing; but smooth handles of uniform dimensions are often formed by pressure through an aperture of corresponding shape and diameter. The union of all such parts with the body is effected by sticking them together under very gentle pressure, the two opposing surfaces having been previously roughened and covered with slip. All changes which affect unequally the mass of the vessel and the ornamental parts tend to cause cracks during the drying, and to separate the latter. It is therefore essential that the body and the ornamentation of the vessel be equally dry, and that the surfaces be prepared either by turning or casting in the same manner; also, that all excess of slip, from the increase of moisture it contains, be avoided. The same precautions apply to the joining together of pieces moulded in separate forms, the surfaces of which should be retouched with a sponge or wet cloth.

Firing.—In the operation of firing the true porcelain with the glaze is rendered dense, vitreous, sonorous, and translucent. The waste heat from this process is employed for the firing previous to glazing.

Porcelain, like many other kinds of clay wares, is always, therefore, inclosed during firing within clay vessels or *saggers*, to avoid the direct action of the flame. The temperature of the furnace must, for the successful firing of the pieces, be maintained as steady and uniform as possible, otherwise various misfortunes, such as splitting, bending, and fusing, will ensue.

The porcelain furnace is in form very similar to the glass furnace, with the exception that the source of heat is dispersed over several grates situated at the circumference of the base instead of being united into one central fire. It consists of a round chamber, on the floor of which the saggers containing the ware are arranged and piled in columns or *bungs*, the flames ascending from a number of wide flues below and around, in connection with the same number of fire-places, so as to circulate between the columns of saggers, filling the whole space, and escaping through different apertures at the top of the chamber into a second room, where they are again employed for heating the *biscuit-ware*.

Kilns for true porcelain are much more durable than glass furnaces, being free from the destructive action of the volatile alkalies; on an average they last 300 firings, while in some places they have endured a much longer period. A dry foundation, exerting as little cooling influence as possible, is an important point in their construction.

After the chambers of the furnace have been properly charged with saggers, the apertures are all closed, and the process of *firing* commences. In this process there are two distinct stages—the first intended only to expel the moisture which may still remain in the vessels, and gradually raise them to a red heat, while the second completes the baking of the porcelain. In general the baking occupies from seven to eight hours, and the firing from eleven to thirteen. In some instances the two processes, as at Berlin, are nearly the same, the one taking from twelve to fifteen hours, and the firing from seventeen to eighteen. At Sèvres, again, the first is the longer process, occupying from fifteen to eighteen hours, while the baking only takes from ten to twelve hours.

In consequence of the glaze of porcelain being a true glass, and entering into the mass, the process of annealing is required—that is, the material must be cooled slowly, in order to prevent it becoming brittle. It is not necessary to employ any separate kiln for the annealing process, the kiln, with its contents, being simply bricked up after firing until it has become sufficiently cool to be emptied. A period of from five to eight days is allowed for the gradual reduction of temperature. In general the kiln is opened the evening before the porcelain is removed, the annealing process being thereby rendered more complete.

Saggers. — The composition of which the *saggers* are made at Sèvres consists of 40 parts plastic clay, sometimes decanted, and 60 parts of ground fragments of old saggers, or an equal quantity of a mixture containing equal proportions of fragments and crushed quartz sand. At Meissen 60 parts of clay are used to 40 parts cement; at Berlin 66·7 clay to 33·3 cement. At Sèvres it has been ascertained that the average duration of the saggers is 15 firings or more; at Vienna from 4 to 5; and at Berlin only from 2 to 3; in which latter case the loss occasioned by the saggers becoming useless amounts to nearly 30 dollars, or about £4 10*s.* at each firing. At Meissen 20 per cent. of the saggers are lost at each firing. The saggers are made in the form of shallow cylinders, except when the particular form of the piece requires it otherwise, and the bottom being flat, each sagger forms the lid of the one placed underneath. Several vessels are placed in each one, and in order to insure the wares standing upon a perfectly smooth and even surface, small ground plates are introduced, consisting of the same material as the saggers, and which can be easily taken away and repaired as required. In order to prevent the ware adhering to the plate, the glaze is removed from those parts of the piece that come into contact with it; and as even those parts which are free from glaze are liable to soften and adhere, sand is interposed to prevent this occurring. Saggers which are intended to support hollow wares, such as plates, pans, saucers, &c., are constructed with a curved bottom, which, projecting downwards into the hollow of the vessel situated in the sagger beneath, economizes space.

After firing the wares are removed from the saggers, and the sand which may have attached itself to their bottoms, where they rested on the saggers, is ground off by a piece of sandstone or some such substance, used as a kind of file; while those articles which have been spoilt by bending are assorted and placed aside. This warpage of the ware is sometimes of considerable amount; at Vienna, for example, only three plates out of four come perfect and sound from the firing.

The Glaze.—At Sèvres the glaze is composed of the pegmatite from St. Yrieix, which is felspar incorporated with a certain proportion of quartz. Although the proportions of these two constituents may vary considerably in small pieces, this ceases to be the case in the enormous mass prepared at the same time at Sèvres, as shown by the following table:—

Component Parts of the Glaze.	Berthier.	A. Laurent.	Malaguti.	Marignac.	Salvetat.
Silica,	73·0	74·0	73·4	74·6	74·3
Alumina,	16·2	18·6	15·7	16·0	18·3
Potash,	8·4	6·6	7·4	8·1	6·5
Lime,	—	0·4	1·9	1·2	0·4
Magnesia,	—	0·3	0·3	—	0·2
Loss by water,	0·6	—	1·3	—	0·3
Loss,	1·8	0·1	—.	0·1	—
	100·0	100·0	100·0	100·0	100·0

The mean of these analyses corresponds with the formula—

$$2(Al_2O_3.3SiO_2) + K_2O,3SiO_2.$$

In some places, as at Berlin, Nymphenburg, and Meissen, the glaze is composed of kaolin, gypsum, and broken porcelain, equivalent to a glaze containing alumina and lime, with no more potash than the small quantity contained in the felspar of the kaolin and broken porcelain. As has been before stated, all the ingredients of the glaze require to be finely pulverized, decanted, and mixed in the same manner as the paste composing the ware. The operation of putting on the glaze can only be accomplished in a rapid and uniform manner by dipping the pieces into a vessel containing the glaze in the form of slip suspended in water; and as in this operation the wares, if simply dried, would not only be liable to bend in handling, but would also absorb the water too slowly, they are previously fired to a certain extent, in which state they are called *biscuit;* and after having received this first firing, they absorb, when dipped into the mixture, a certain quantity of water, leaving the suspended glaze attached to the surface. In general, a very short immersion, varying from twenty to forty seconds, is sufficient; the more rapidly that the operation is performed, the more uniform will be the absorption of the liquid; and to insure this as far as possible, that portion of the ware which was first dipped into the glaze is always first removed. After the dipping process has taken place, the part of the piece held by the workman is coated with glaze by the aid of a brush, and the glaze is removed from those parts of the vessel which, coming in contact with the sagger in the operation of firing, might cause adherence by its fusion.

Vinegar exerts a most remarkable influence in preventing precipitation of the slip; for instance, glaze in water at a temperature of 68° Fahr. requires only four hours and twenty minutes to separate; in water, at a temperature of 140° Fahr., three hours; while in water containing three-seventh parts of vinegar it requires six hours; and in water with one twenty-secondth part of gum-arabic eight hours, under similar circumstances. These are, therefore, always added.

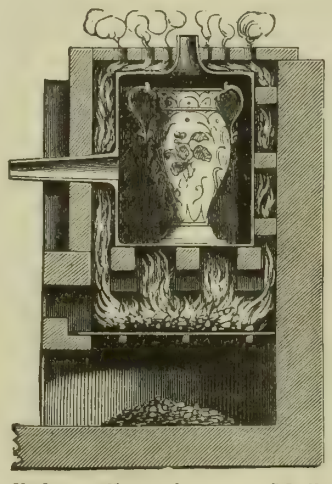
Painting.—The surface of porcelain being that of a true glass, it is the best adapted of all clay wares for the purposes of ornamentation with pigments and metallic lustres; the art being analogous, in fact, to glass-painting, with the difference that the colouring is solely adapted for reflection, and not for effect by transmitted light. All the pigments, therefore, are coloured glasses, which acquire their lustre and adhesion to the mass by fusion, and consist of a *flux*, with the addition of colour, generally a metallic oxide. Some of the metallic combinations in use for producing the various hues are given below:—

Yellow,	Oxide of titanium.
Yellow,	Chromate of lead and chromate of barium.
Yellow—different tints,	Oxide of antimony.
Orange-yellow, black,	Oxide of uranium.

Yellow tints—red, brown, violet, grey, sepia, black,	Oxide of iron.
Violet, brown, black,	Manganese dioxide.
Blue, grey, black,	Oxide of cobalt.
Brown,	Ferrous chromate.
As an addition to carmine and purple,	Chloride of silver.
Purple,	Purple of Cassius.
Red,	Cuprous oxide.
Green,	Cupric oxide.
Green,	Chromic oxide.

Transparent and opaque colours or enamels are used with equal effect. Transparent colours are rendered *opaque* by the addition of oxide of tin; and oxide of zinc is used for *enlivening* the different tints. The colours are classified according to the reaction of the temperature upon their constituents, being divided into such as have the power of withstanding the most intense heat of the firing kiln, and which can be burnt in with the glaze—termed refractory colours, and those which require to be applied to the wares after the process of glazing has been completed, and afterwards fixed in a small furnace called the *muffle*, shown at Fig. 2—and are

Fig. 2.



hence called muffle colours. *Muffle* colours, being painted upon the ware in *relief*, can be distinguished by touch from the decoration in *refractory* colours. The refractory colours are—

Blue, with cobalt.
Green, with chromium.
Brown, with oxide of iron, manganese dioxide, and perferric chromate.
Yellow, with oxide of titanium.
Black, with oxide of uranium.

These pigments generally impart a very intense colour, and can be used in very small quantities; they exert no liquefying action on the glaze or on the mass of the ware. They may either be applied directly to the biscuit ware or upon the glaze, the silicate of an alkali being used with them as a flux. *Muffle* colours are incorporated with a great variety of fluxes, the most important of which are—sand or quartz, saltpetre, borax and boracic acid, felspar, potash, soda, and minium or litharge.

Gilding is executed on porcelain thus:—The gold is precipitated from its solution in nitrohydrochloric acid by ferrous sulphate. The brown powder obtained is washed, dried, mixed with about one-tenth of oxide of bismuth, and rubbed up with thickened oil of turpentine. This gold mixture is then applied with the brush and fired in the usual manner, when the oxide of bismuth forms a flux with the surface of the glaze, and the gold becomes firmly attached. It has a dull yellow appearance upon leaving the *muffle*, and requires to be burnished with an agate to restore its metallic lustre. A preparation of gold, held in complete solution by oil of turpentine, is used for gilding at Meissen. It is not so durable, however, as that obtained by the ordinary process.

Platinum Black, or *Platinum Sponge*, is applied in precisely the same manner as the metallic gold. As a certain amount of heat is necessary in the muffle for the successful firing of the more fusible colours and gilded ware, pyrometrical tests are applied to ascertain the necessary temperature. A very convenient test is afforded by the variation of colour through which the gold purple passes when submitted to a gradually increased temperature, six gradations being marked by the porcelain painters, corresponding to the six most important changes in temperature. Thus a piece of porcelain painted with the prepared purple of Cassius, and exposed to the muffle, gradually becomes—

			Degrees of Fahr.
Of a dirty-brown red colour,	corresponding to	gilding upon coloured grounds,	1148°
Brick-red, / Brick-red, passing into rose, and red on the edges and thinner parts,	"	retouching,	1474°
Rose-colour, passing into purple,	"	easily fusible colours,	1652°
Rose-colour, passing into violet,	"	gilding upon glaze,	1688°
Rose-colour, passing into deep violet, / Violet has become lighter.	"	gilding upon plate edges, / more difficultly fusible colours,	1742°
Rose-colour has disappeared, and the violet become very pale,	"	dull gilding,	1832°

The process of gilding is as follows:—The gold (which is prepared with quicksilver and flux), when ready for use, appears a black dust. It is used with turpentine and oils similar to the enamel colours, and, like them, worked with the ordinary camel's hair pencil. It flows very freely, and is equally adapted for producing broad, massive bands and grounds, or the finest details of the most elaborate design.

To obviate the difficulty and expense of drawing the pattern on every piece of a service, when it is at all intricate, a "pounce" is used, and the outline dusted through with charcoal—a method which also secures uniformity of size and shape. Women are

precluded from working at this branch of the business, though, from its simplicity and lightness, it would appear so well adapted for them. Firing restores the gold to its proper tint, which first assumes the character of "dead gold," its after brilliancy being the result of another process termed "burnishing."

The *watches* introduced into the muffle for the purpose of ascertaining the temperature are covered both with gold and colour, in order to ascertain the degree of heat at which the gold becomes attached without altering the tints of the hues. Painted porcelain generally requires retouching and passing through the muffle two or three times, according to the degree of finish required by the artist.

At Sèvres, also, an ingenious method of removing faults in the painting is adopted previously to retouching them. A brush, dipped into liquid hydrofluoric acid, is traced over the parts, which are afterwards washed with water; the etched part appearing perfectly white, and only slightly corroded, is in a very favourable condition for receiving the fresh pigments.

A kind of lustred glaze, intermediate between true metallic decoration and the ordinary vitreous glaze, has been introduced by Brianchon, of Paris. His English patent, dated 1857, gives directions for obtaining various iridescent tints on porcelain. The effects produced are similar to those of the famed lustred wares of certain Italian Majolica, but are inferior in richness of hue. Brianchon's process resembles that lately used at Worcester and at the Belleek works in Ireland, where indeed the manufacture of the lustred ware is a distinguishing speciality. In Brianchon's process a flux is first formed by heating together—

10 parts (by weight) of nitrate of bismuth,
30 " resin,
40 " essence of lavender.

When this mixture has cooled slowly, 35 additional parts of essence of lavender are introduced.

With this flux or glaze various colouring substances are to be mixed, according to the special kind of iridescence sought after. For *yellow*, use—

10 parts nitrate of uranium,
30 " resin,
35 " essence of lavender.

On cooling, add 30 parts more essence.

For *orange red*, use—

15 parts nitrate of iron,
15 " resin,
18 " essence of lavender.

On cooling, add 20 parts more essence.

For *imitation gold*, mix together 2 or 3 parts of the uranium liquor with 1 part of the iron preparation. Brianchon also uses for his iridescent glazes such gold salts as the cyanide, the "ammoniuret," and the iodide, in combination with the bismuth glaze, and with the other liquids above described.

W. de Morgan, of the Orange House Pottery, Chelsea, has lately succeeded in obtaining some very decided and beautiful lustred colours on pottery by means of the effect of certain reducing vapours upon pigments rich in copper, silver, &c. His wares have also the further merit of decorative design. They reproduce many of the beautiful effects of the lustred Italian, Persian, and Hispano-Moorish pottery of the sixteenth century.

Parian or Ceramic Statuary.—Ceramic statuary, introduced about 1854, is the finest description of biscuit made, and differs only from porcelain by the employment of a soft, fusible felspar in place of Cornish-stone. The general introduction of this art was first successfully carried out by the late firm of Copeland & Garrett, the eminent manufacturers of Stoke-upon-Trent, under the artistic direction of Thomas Battam, F.S.A., and founder of the Ceramic Art Union, established 1859, for the encouragement of fine art manufactures.

In the *Parian* body the agreeable creamy or yellowish-white tint which it possesses is owing to the presence of a small quantity of oxide of iron in the clays and felspar, which during the firing forms with the silicic acid a ferric silicate. The making of figures with the Parian body requires great care, knowledge, and skill, as they are cast in different parts, and afterwards united. The *slip* for this purpose is in a liquid state, the deposit in the mould being allowed time to harden before removal, after which those parts which, from the softness and yielding of the mass, might sink, are supported by props. From the large proportion of moisture contained in the slip, the mass contracts in the firing process no less than one-fourth of its bulk. Some of the ingredients composing the finest Parian body are given below:—

No. 1.—Frit.

	Lbs.
Well-washed Lynn or Isle of Wight sand,	80
Felspar,	35
Cornish-stone,	15
Pearl-ash,	12

The whole mixed together with water, and fired in flinted saggers, at the earthenware heat.

Mass.

Frit,	50
Felspar,	130
China clay,	130
Fine powdered glass,	20

These ingredients being all well ground together.

No. 2.—Frit, made as before.

Mass.

Frit,	50
Felspar,	35
Felspar calcined at a gloss heat,	35
China clay,	75
Bone,	75
Powdered glass,	15

Beautiful perforations and network, such as lace, drapery, &c., are made by dipping the original fabric into the slip. The subsequent process of firing destroys the original tissue inside. In practice the process may be described as follows:—Upon a gypsum slab, over the surface of which a film of the

slip has been brushed, the piece of net is evenly spread out and a second coating of slip afterwards laid over the whole. The porosity of the gypsum absorbing the water leaves only the clay in a thin film surrounding the fibres of the net, which, when lifted, is wrapt around the statuette to be decorated, and placed in the oven.

STONEWARE.—The mass composing fine stoneware is a mixture of plastic clay and a flux of a felspathic nature. The hard texture of plastic clay after burning, and the shrinking it undergoes, cause it to become very fragile, while the application of long and intense heat is necessary to produce that semi-fusion which is one of the characteristics of the ware. This semi-fusion is facilitated by the addition of the flux, which acts precisely in the same manner as in real porcelain; the chief external difference between fine stoneware and real porcelain being the almost entire absence of translucency in the former.

Mixture.—The mass composing the body of fine stoneware is distinguished by the term *dry body*. It is generally composed of *kaolin*, *plastic clay*, and *Cornish-stone* as a flux, sometimes the kaolin, and sometimes the plastic clay taking the preponderance; but the proportion of the flux generally amounts to 50 per cent. of the whole—a much larger proportion than in the true porcelain body. It is from this cause that fine stoneware, when subjected to the heat of a porcelain kiln, melts, and requires therefore a more moderate temperature in baking. The mass is much more plastic than that of true porcelain, a circumstance which enables it to bear a much larger proportion of a poor flux, such as felspar, than the kaolin. Some of the proportions in mixing the mass are given below:—

White Stoneware Bodies for Jugs, &c.	I.	II.	III.	IV.
Cornish-stone,	80	40	100	30
Cornish clay,	20	10	20	10
Blue clay,	40	20	18	17
Flint,	20	—	40	2

With the addition of a little blue cobalt to whiten.

Mortar Bodies.	I.	II.	III.	IV.
Cornish-stone,	200	90	50	50
Blue clay,	80	80	25	20
China-clay,	—	30	20	40
Glass,	—	—	1	—

These separate ingredients are all ground to a fine powder and mixed together with the greatest care, in order to increase the plasticity of the mass in working.

The wares are formed by means of the *wheel* and *lathe*, or are pressed into plaster of Paris moulds, when the irregularities of the outline render this necessary. Many kinds of this ware are decorated with *basso-relievos*, which are fixed on to the body. Many varieties of stoneware are stained by metallic oxides. The ingredients in use for forming *sage*, white stoneware body, are oxide of chrome and cobalt; *drab*, white stoneware body, 15 per cent. common marl and a little nickel; *dove*, white stoneware body, 1 per cent. manganese with one-fourth part per cent. cobalt.

Wedgwood Jasper Wares.—Amongst this celebrated description of fine stoneware, the manufacture of WEDGWOOD, may be enumerated those known as *jasper*, *terra-cotta*, *basalt*, *granite*, and *porphyry*.

One of the most remarkable of these bodies is the *jasper* or *onyx*, a white biscuit, which has the property of receiving through its entire mass, by the admixture of metallic oxides, the same colours that those oxides would impart to glass or enamel in a state of fusion.

The composition of this jasper or onyx body may be given as follows, the blue colour being imparted by the admixture of oxide of cobalt, in proportions varying from one-third of a part to one part per cent., or more, according to the depth of tint required:—

White Jasper Bodies.	I.	II.	III.	IV.	V.	VI.
Sulphate of barium,	150	40	30	50	32	160
China-clay,	35	—	—	15	10	60
Blue clay,	45	20	12	35	25	90
Flint	35	—	3	10	8	40
Gypsum,	6	—	—	—	1	8
Cornish-stone,	50	20	20	—	7	—
Bone,	—	—	—	25	—	—

The proportion of *stain* is one part of cobalt to from 50 to 75 parts of the body, according to the depth of colour required. The various other coloured jaspers are obtained by the addition of other oxides to the several white bodies. The *green* jasper is obtained by the admixture of the oxide of chromium.

In wares of this description the mass is frequently white, and only covered on the surface with a thin coloured coating of the same body, the shrinking properties of the mass not being essentially affected by the addition of small quantities of the metallic oxides. The mass, after formation upon the throwing wheel in the usual manner, receives when sufficiently hardened the proper outline upon the lathe; and if a vase or other similar shape, such rims or fillets are turned as are intended to appear white upon the dark ground in the after manipulations. The piece is then taken into the dipping-room, where it is immersed in a tub containing the coloured slip of a consistency approaching thick cream, and receives a thin even film over its whole surface. It is then allowed to harden until it is sufficiently firm to admit of being placed a second time upon the lathe, when a burnisher is run over it to give uniformity and smoothness to the surface; the blue dip, at the same time, being turned off, and exposing those portions intended to appear white.

The piece is then taken to the *decorator*, who affixes the various ornamentations intended to complete the design. Taking the vase in one hand, he with a small hair pencil moistens with water that portion of the surface intended to receive the pattern, which is affixed in its proper position by a very gentle pressure of the finger, and the aid of a damp sponge; each separate ornament being added in this manner, until the whole decoration is complete. The piece is then sent into the oven to be fired in the usual way

The ornaments in relief are obtained, like an impression from a seal, by pressure in a mould made of baked clay or plaster of Paris. The moulder sits at a bench with a number of these small moulds before him, a lump of the plastic material forming the body of the ware being placed at his side, and from which, by means of a small spatula, he separates pieces of the clay, and rapidly fills or presses them into three or four of the moulds. This done, he takes the one first in order, and with the smooth flat end of his tool burnishes over the surface of the mould, removing the surplus clay, and causing the sharp-cutting edge of the die to give a clean sharp outline to the impressed clay, which, yielding slightly to the rubbing process by suction, leaves the mould, and is turned out on a slab for use by the decorator.

Basalt or Black Egyptian Biscuit.—Many articles of domestic requirements, such as tea-pots, milk-jugs, &c., are moulded from this mass. In composition it may be given as follows:—

Basalt or Black Egyptian Bodies.	I.	II.	III.	IV.	V.	VI.
Blue clay,	200	330	200	—	100	—
Red clay,	—	—	300	500	—	500
Ochre calcined,	200	300	100	75	100	—
Iron scales,	—	30	—	—	35	—
Manganese,	60	80	100	75	40	100

Red Body—Terra-cotta Ware.

Red marl very carefully sifted, ... 10 parts.
Common marl, ... 2 "

with the addition of 10 per cent. of Cornish-clay, if a light colour is required.

Fine stoneware in general is never glazed, though at times a glaze is produced spontaneously with the firing by a process called *smearing*, the inner surface of the saggers being coated with a glaze composed of *fine white stoneware.*—No. 1—Lead, 6; stone, 3; salt, 3. No. 2—Flint, 10; bone, 5; nitre, 3; salt, 5. No. 3—Lead, 4; stone, 1; salt, 2; flint, 1. No. 4—Glaze, 4; salt, 1; potassa, ½. No. 5—Calcined bones, 3; common salt, 1. No. 6—Bones, 5; salt, 3; No. 7—Flint, 10; bones, 5; salt, 5; nitre, 3.

Wash Smears.—Lime at 24 ozs., 3 quarts; slip at 24 ozs., 2 quarts; salt, 2 lbs.; nitre, 1 lb. The ingredients are dissolved in hot water, and the saggers washed inside with the mixture.

This in part becoming volatilized during the firing, a portion of the alkali and oxide of lead is absorbed by the surface of the ware, forming a thin layer of glaze, both the surfaces containing silica appropriating a fair proportion of the vitrifiable bases. Sometimes a glaze containing a large quantity of lead or borax is applied to either both or only one surface of the ware. When pigments are mixed with the glaze, colours are communicated to the ware. The firing of this kind of ware takes place in saggers in the ordinary furnaces.

In the manufacture of ordinary stoneware vessels the process of decanting the clay from water would be too costly; the coarser impurities are therefore either removed by repeated kneadings and treading out of the mass by manual labour, or separated by passing the clay through a *pug-mill.*

The low price at which these wares are sold in the market necessitates the adoption of the most simple modes of forming and manipulation; they are generally, therefore, thrown upon the potter's wheel, which is generally turned by steam power.

The kiln is in general of a very rough construction, being simply a huge reverberatory furnace. The wares are introduced into the kiln by doors, which are bricked up during the firing. At Lambeth, near London, the kilns are vertical, are about 10 feet in diameter in the baking chamber, and 11 feet high to the centre of the crown; they have five fire grates, each 12 inches wide and 3 feet long, containing five or six fire-bars, a bag or chimney flue about 5 feet high being placed opposite each fire. Great care is required in the management of the fires, as, if too little air is admitted, the smoke and gas will be imperfectly consumed and the wares discoloured; while, on the contrary, if air enters too freely the heat is not sufficiently intense to vitrify the clay.

Common stoneware, being sufficiently dense and vitreous in its mass to be impermeable, is glazed by a very cheap and simple process. The waste from other branches of the manufacture is ground to a fine powder, and sifted or sprinkled over the moist ware in a thin stratum; it is afterwards burnt on in the process of firing. Iron slag is generally used for this purpose.

The simple and old-fashioned salt-glaze is also of very general application. The process takes place towards the end of the firing, when salt is thrown into the kiln through particular apertures. The temperature of the kiln being considerably above a red heat, volatilizes the sodium chloride into a vapour which, filling the chamber, surrounds the wares, and causes a reaction to take place with the silica of the mass—a change which is approximately represented in the equation:—

$$2NaCl + xSiO_2 + H_2O = Na_2OxSiO_2 + 2HCl.$$

The glaze is a soda glass, and exists as a very thin coating upon the surface of the wares. Clays which contain less than 50 per cent. silica do not decompose salt. A brown colour is given by throwing into the furnace, during the glazing process, substances which afford a large volume of smoke, such as the bark of the birch tree.

Common stoneware generally varies in colour from grey to bluish-grey, yellowish-red, brownish-red, and brown.

EARTHENWARE.—Under the term *earthenware* are embraced those varieties of pottery which on fracture have an earthy appearance, are perfectly opaque, and are coated with a soft, easily fusible glaze, containing lead or borax.

Fine Earthenware.—The English manufacture is composed essentially of a mixture of plastic clay and quartz. The crude materials are Cornish-stone and china-clay. The class called *ironstone china* is made from a mixture of plastic clay, kaolin, Cornish-stone in excess, and silica, the formula of which is subjoined:—

IRONSTONE CHINA BODIES.

	I.	II.	III.	IV.	V.	VI.
Cornish-stone,	180	200	700	600	600	400
China-clay,	120	150	500	600	100	250
Blue clay,	60	100	300	—	180	150
Flint,	80	120	250	400	60	75

A small proportion of cobalt blue is added as a stain to whiten the mass.

These are the three principal modifications into which this class of clay wares may be subdivided, leaving innumerable others of an intermediate character. Mixtures for the mass of the following varieties are given below:—

CREAM-COLOURED WARE BODIES.

Slip Mixtures by Measure; Dry Mixtures in Parts.

	Dry Mixtures.		Slip Mixtures in Inches.		
Blue clay,	22	12	11	13	12
China-clay,	9	12	6	3½	4
Flint,	5½	10	4	2¾	3
Cornish-stone,	—	—	3¼	¾	—

Turquoise Body.

Blue clay,	300 lbs.
China-clay,	175 "
Flint,	200 "
Cornish-stone,	60 "
Turquoise stain,	20 "

Turquoise stain consists as follows:—

Blue cobalt,	1 lb.
Flint,	2½ lbs.
Oxide of zinc,	10 "

Calcined together in earthenware biscuit oven, and finely ground for use.

Pale Drab Body.

Fine white earthenware body,	700 lbs.
Stain—nickel,	4 "
Cobalt calx,	1¼ lb.

Buff Body.

Finely ground grey marl,	100 lbs.
Fine earthenware body,	100 "

Inside Wash for above Coloured Bodies.

China-clay,	40 lbs.
Blue clay,	20 "
Flint,	20 "
Cornish-stone,	10 "
Cobalt calx, to whiten,	15 drachms.

This wash is poured smartly into the interior of the ware after forming, and immediately emptied.

COLOURED CLAYS FOR ORNAMENTATION.

Turquoise or *blue*, take of the body of the ware 40 lbs., and 1¼ lb. of the turquoise stain.

Green Clay.

Body,	40 lbs.
Nickel,	3 "
Cobalt calx,	¾ oz.

Drab Clay.

Body,	60 lbs.
Nickel,	12 ozs.
Cobalt calx,	3 "

Dark Chrome Green Clay.

Body,	40 lbs.
Oxide of chrome,	3 "

Orange Clay.

Body,	40 lbs.
Fine red marl,	20 "
Flint,	7 "

In general use for moulding and pressing.

FINE EARTHENWARE BODIES.

In Slip by Measure.

	Slip Mixtures in Inches in Tub.				
	—	1.	2.	3.	4.
	Ozs. to the Pint.	Inches.	Inches.	Inches.	Inches.
Blue clay,	24	7½	12½	7	9
China-clay,	26	9	5	9	7
Flint,	32	3	3	5½	5
Cornish-stone,	31½	½	—	2½	3

Dry in Parts.

	1.	2.	3.
Blue clay,	200	500	500
China-clay,	200	800	650
Flint,	200	800	450
Cornish-stone,	75	300	200

TERRA-COTTA, OR POROUS BODIES FOR WATER BOTTLES, &c.

	Green.	Blue.
Earthenware body,	100	100
Cornish-stone,	15	10
Oxide of chrome,	3	3

	Red.
Dark red marl,	300
Blue ball clay,	100
Turquoise stain.	

	Cane.
Grey marl,	120
Blue clay,	13
Flint,	6

The marls should be very carefully sifted through fine lawns; and if ground finely in a pan at the mill, the body will be much improved. This remark applies to all coloured bodies. These porous bodies are all fired in the glazing oven.

The Mass.—The flints are calcined, crushed, and finally broken to powder under water.

The Cornish-stone is ground, but without calcination; it is used in the bodies and glazes.

To increase its plasticity, the china or Cornish clay is mixed with as much blue clay as the quality of the ware admits. The liquid with the clay in suspension is decanted, and passes into vats in the *mixing* or *slip house*. The china-clay and blue ball clay having been admitted into the tanks severally, in due proportions, are united in the mixing cistern. The relative proportions by measure of Cornish-stone and flint are next added, and mixed with the mass, which then passes through a set of fine silken sieves, fixed in a frame, to which a sifting motion is imparted. This causes a complete filtration of the slip, all the coarser impurities being left behind.

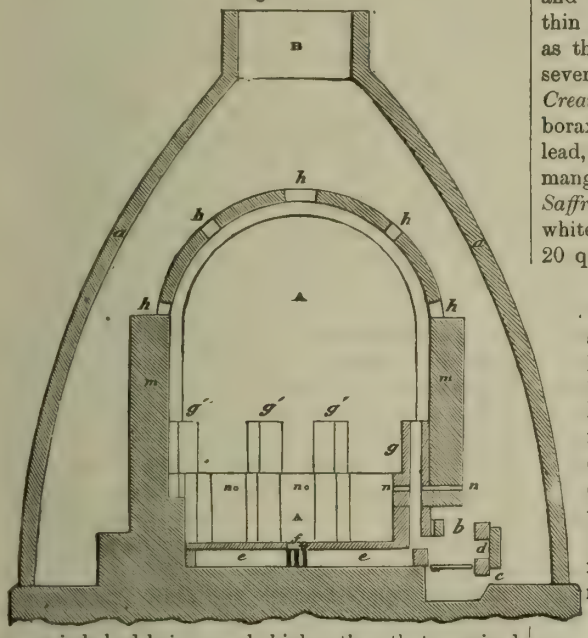
The slip was formerly consolidated by heat; this is now usually effected by hydraulic pressure. It next passes through a *pug-mill*, to bring the mass to a uniform consistency. The mill consists of a circular iron vat or cylinder, bound together by iron hoops, through the centre of which an iron shaft revolves, carrying with it several horizontal arms, armed with the sharp blades; these are fixed horizontally, and inclined at a certain angle. By this arrangement the clay in its passage through the mill is cut up and forced out at the bottom of the mill.

The clay as it issues from the machine is cut, by means of a fine wire, into blocks, which are carried away to the store-house for the process of *ageing*. Before the mass is placed in the *thrower's* hands it undergoes a further stage of preparation, termed *slapping* or *wedging*, by being forcibly thrown upon a strong slab of plaster of Paris.

Throwing.—From the much greater plasticity of the mass used for earthenware, the operation of throwing upon the wheel is one of great rapidity. The potter's wheel and lathe are moved by machinery.

Firing.—The temperature at which fine earthenware is baked being much higher than that required for the glaze, renders it necessary that the vessels should be fired twice. At the first firing the ware is completely baked, or converted into biscuit, the glaze being burnt on in the second firing. Two separate furnaces are employed for these distinct operations. The kiln used for baking—Fig. 3—has only one chamber, A, and is surrounded by a conical brick building, *a a*, termed a *hovel*, that serves at once the purpose of roof and chimney. The construction is nearly the same as that of an upright reverberatory furnace. The fuel is coal. The draught is regulated by the aperture, *b*, and passes into the furnace in a downward course, carrying with it the flames in a horizontal direction; *c* is the opening for removing the cinders, and *d* that by which fuel is introduced into the furnace. The flame, before entering the chamber of the furnace, is divided; part of it passes through channels below the sole of the furnace, along the horizontal flues, *e*, and enters at the central point, *f*, the remainder circulating upwards through the small chimneys or bags *g*, situated against the wall, *m*, of the kiln, A. Each fire, of which there are six or eight, has a corresponding chimney, *g' g'*, and horizontal flues converging towards *f*, and becoming narrower as they approach the centre. The flame finally escapes through the openings, *h h h*, in the dome of the chamber, A, and out of the top of the hovel, B. The small openings, *n n*, are for the removal of the *watches* from the saggers placed opposite, and by which the potter ascertains the state of the kiln. The height of the chamber, A, averages about 18 feet, the diameter about 16 feet.

Fig. 3.



The wares are always inclosed in saggers, which are arranged in the kiln in columns or bungs after the manner described under *Porcelain*.

Glaze.—The various ingredients are mostly fused together or fritted, and afterwards ground, sieved, and purified. The materials being formed into a thin water fluid, the process of glazing is the same as that described under *Porcelain*. Subjoined are several mixtures of glazes:—RAW GLAZES—*Common Cream Colour Glaze.*—Cornish stone, 150; flint, 35; borax, 4; white lead, 300. *Rockingham Glaze.*—Red lead, 42; Cornish stone, 6; flint, 4½; China clay, 4½; manganese, 6; ground finely for use. *Yellow or Saffron Glaze.*—Underglaze yellow colour, 10 lbs.; white lead, 20 lbs., very finely ground; add to which 20 quarts of cream colour glaze (4¼ lbs. per quart), well sifted together. *Chrome Green Glaze.*—Chrome oxide (green), 2 lbs.; flint glaze, 4 lbs.; ground for stain; add to which 48 quarts of printed glaze (28 oz. per pint), and well sifted together. *Dessert Green Glaze.*—White lead, 3 lbs.; calcined copper, 3 lbs.; flint glass, 1½ lb.; flint, 2 lbs.; finely ground together. And mix of the above, 4 quarts; printed glaze, 12 quarts; cream-colour printed glaze, 9 quarts; earthenware slip, 3 pints; well lawned together. *Black Glaze.*—White lead, 50; Cornish stone, 20; flint, 10; China clay, 7; manganese, 10; ground for dipping.

PAINTED WARE GLAZES—FRITTED.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Cornish-stone,.	100	180	80	90	40	50	120	100	120
Felspar,.....	—	—	—	—	40	—	—	—	—
Flint,.....	60	100	70	5	—	35	70	20	80
Lynn sand,.....	—	—	—	—	30	—	—	—	—
Whiting,.....	25	—	—	—	—	40	30	30	80
Chalk,.....	—	—	25	—	15	—	—	—	—
Tincal, ...	—	120	—	—	—	—	—	—	—
Borax,.....	70	—	75	65	60	100	75	60	120
China-clay,.....	10	10	—	25	—	30	10	—	30
White lead,....	60	—	—	—	—	—	—	—	—
Red lead,.....	—	—	—	—	—	—	30	—	—
Soda, ...	—	—	—	25	—	—	10	15	20
Fritted in kiln, and mixed as follows:—									
Cornish-stone,.	60	—	100	150	160	35	75	100	180
White lead,....	60	100	100	200	160	45	60	—	120
Whiting,.....	—	80	—	80	—	—	—	—	—
Flint,.....	—	—	—	80	—	35	—	—	70
Frit, ...	500	300	300	180	300	240	500	300	300

The frit is withdrawn from the kiln when in its molten condition, and thrown or run into cold water. When the dipped biscuit has become sufficiently dry, the glaze is burnt in, being placed in saggers similar to the biscuit saggers, and glazed on their inner surface. The time occupied by the firing of the glaze kiln is about sixteen hours.

FRITTED GLAZES.

Cream-Colour Glaze.

	I.	II.	III.	IV.
Cornish-stone,	180	200	—	50
Flint	60	50	50	80
Flint glass,	50	75	50	—
White lead	600	350	200	260
Frit,	—	—	100	—
China-clay,	—	—	—	45
Whiting,	—	—	—	45
Frit composed of Cornish-stone,	20	} Calcined in gloss oven.		
Frit composed of soda,	1¼			

Printing.—The process of printing consists of two parts—first, the production of an impression upon thin paper in a suitable ink, and then transference of the ink upon this paper to the surface of the biscuit. The vehicle which serves as the preparation for embodying the necessary colours is a composition formed of boiled linseed oil, resin, tar, and oil of amber, and which becomes, when mixed with the colours, sufficiently liquid for use by spreading out upon a hot iron plate.

Underglaze, Printing, and Overglaze Colours for Earthenware—*Yellow.*—Lead and tin ash, 4 parts; antimony, 1 part; mix well together, and calcine at a gentle heat in a glazing oven; to undergo a second calcination at a higher temperature in the same oven. *Orange.*—Antimony, 3 lbs.; litharge, 3 lbs.; lead and tin ash, ½ lb.; ochre calcined, 3 ozs.; calcination as above. *Fine Brown.*—Chromate of iron, 1 lb.; chromate of lead, ¾ lb.; calcined sienna, 2 lbs.; oxide of zinc, 3 lbs.; calcine only once. *Brown.*—Oxide of manganese, 4 lbs.; green oxide of chromium, 1¼ lb.; Cornish-stone, 4 lbs.; well calcined. *Yellow Green.*—Flint glass, 4 lbs.; whiting, 2½ lbs.; green oxide of chromium, 1½ lb.; calcined at biscuit oven heat, and well pounded, washed with boiling water until clear, and calcined a second time. *Yellow Green.*—Green oxide of chromium, 3 lbs.; yellow colour, 3 lbs.; china-clay, burnt at biscuit heat, 2 lbs.; fine sand, 2 lbs.; calcined together. *Blue Green.*—Green oxide of chromium, 10 lbs.; oxide of cobalt, 2 lbs.; flux composed of equal parts of borax and flint, 15 lbs.; calcined together in biscuit oven. *Rose Colour Pink.*—Oxide of tin, 2¼ lbs.; whiting, 1 lb.; green oxide of chromium, ½ oz.; Cornish-stone, 6 ozs.; calcined in biscuit oven. *Pink.*—Oxide of tin, 100 parts; chalk, 34 parts; oxide of chromium, 1 to 1¼ part; chromate of potash, 3 to 4 parts; silica, 5 parts; alumina, 1 part. *Purple.*—To 15 lbs. of rose colour pink add 1 lb. of cobalt calx and 1½ lb. of fine sand. These proportions may be varied according to that required. *Black.*—Oxide of chromium, 6 lbs.; calcined manganese ore, 9 lbs.; cobalt calx, 7 lbs.; gold litharge, 10 lbs.; calcine in glazing oven. *Black.*—Calcined chromate of iron, 12 lbs.; cobalt calx, 1 lb.; calcine together. *Blue for flowing.*—Black prepared oxide of cobalt, 12 lbs.; flint glass, 4 lbs.; oxide of zinc, 2 lbs.; calcine in glazing oven. The above for strong colour, to be reduced for weaker tints by a flux composed of equal parts of flint glass and flint. *Blue for ordinary printing.*—Blue cobalt calx, 1 lb.; Cornish stone, 1½ lb.; grind for use. Or a mixture of half stone and half flint. May be reduced to 1 part of blue and 5 parts of fluxing material. The fluxing of these blues are much varied by manufacturers.

The colour varnish is prepared as follows:—Mix together 2 gallons linseed oil, 1 quart of rape oil, 2 ozs. red lead, and 1 oz. flowers of sulphur; heat over a fire till adhesive and spongy, upon which mix in 2 lbs. Burgundy pitch, 1 quart naphtha, 1 oz. gum mastic; stir for fifteen minutes, and strain through a hair sieve. The colours are then ground, as in the case of ordinary printers' ink.

The process of applying the pattern to the biscuit is as follows:—The design is engraved upon a copper plate in a broad open style, to prevent the lines from running into each other, and forming a blurred appearance. Those portions intended to produce a shaded effect are cut deeper to retain more colour. The ink, which is first spread over the surface by a printer's dabber while the plate is on the hot stove, is, after the pattern is well filled in, removed by passing a knife over the surface, and wiping with the boss to clean the surface from superfluous oil. The impression is then taken from the plate after the manner of ordinary copperplate printing.

The paper upon which the impression is taken is about the consistency of tracing paper, and previous to use is saturated with soft soap and well damped. After the patterns are separated by scissors, they are placed with the printed side next the ware, and rubbed down upon it with the end of a firmly bound roll of flannel. This is done gently at first, and afterwards more forcibly, until the ink is transferred to the surface of the biscuit. The ware is then plunged into water, when the paper is easily removed after a short time by the gentle application of a sponge.

Bat Printing.—There are two distinct methods of printing in use for china and earthenware—one is transferred on the "bisque," and the other on the glaze. The latter is called "bat printing," and is done on the glaze; and the engravings are for this style exceedingly fine, and no greater depth is required than for ordinary book engravings. The impression is not submitted to the heat necessary for that in the bisque, and the medium of conveying it to the ware is also much purer. The copper plate is first charged with linseed oil, and cleaned off by hand, so that the engraved portion alone retains it. A preparation of glue being run upon flat dishes, about a quarter of an inch thick, is cut to the size required for the subject, and then pressed upon it; and being immediately removed, draws on its surface the oil with which the engraving was filled. The glue is then pressed upon the ware, with the oiled part next the glaze; and being again removed, the design remains, though, being in a pure oil, scarcely perceptible. Colour, finely ground, is then dusted upon it with cotton wool; and a sufficiency adhering to the oil, leaves the impression perfect, and ready to be fired at the enamel kilns.

After printing, the oil is destroyed by heat before the glaze is applied—a process technically termed *hardening on.*

When the printed pattern is applied to the ware above the glaze, the mordant receives a larger proportion of gum mastic; but where enamelling colours are used for the muffle, a *size* is applied to the surface of the glaze, composed of spirits of turpentine, with a small portion of gum mastic dissolved in it, sometimes rosin and sugar of lead being added.

The ornamentation of fine earthenware by hand on the glaze is executed by artists expressly trained for that purpose, and each excelling in a particular branch of ornamentation, as flowers, foliage, scrolls, and the like.

The preparation of suitable pigments for such painting on porcelain and pottery is now carried on in several establishments, both in England and the Continent. These pigments are frequently tinted, so as to present, when moist, some approach to the hue which they will acquire when burnt in the enamelling kiln. They are mixed with fat or resinified oil of turpentine, and thinned as required with spirits of turpentine.

QUININE.—This alkaloid is found naturally in the bark of several species of *cinchona*, which inhabit the eastern slopes of the Cordilleras, in Bolivia, Peru, and New Granada. The cinchonas number some 36 species (HOOKER and BENTHAM). They are all natives of South America. The plants flourish best at from 5000 to 8000 feet above the sea level. The barks of commerce comprise—*Cinchona officinalis* (HOOKER), *C. Calisaya* (WEDDELL), *C. succirubra* (PAVON). These are large evergreen trees with finely-veined leaves. Peruvian bark was introduced into Europe about 1630. It came into use in England about 1655.

The collection of the bark is effected by bands of half-civilized Indians under the direction of collectors, styled *Casadores*. The tree chosen is cleared of its parasitical climbing plants; and after being well beaten, has its outer layer of sapless bark removed. In order to detach the valuable inner bark longitudinal and transverse incisions are made as high as can be reached on the stem. The tree is then felled, and the peeling completed. In most cases, but especially if previously beaten, the bark separates easily from the wood.

In many localities the bark has to be dried by a fire made on the floor of a hut, the bark being placed on hurdles above. In Southern Peru and Bolivia even the thickest calisaya bark is dried in the sun.

The thinner bark as it dries rolls up into tubes, called *canutos* or *canutillos*, while the pieces stripped from the trunks are made to dry flat by being placed one upon another, and loaded with weights; these are known as *plancha*, or *tables*. The bark of the root is also brought into the market.

After drying, the barks are assorted according to size, or are all packed without distinction in sacks or bales. The dealers in the export towns inclose the bark in *serons* of raw bullock hide, which, contracting as it dries, compresses the contents (100 lbs.) of the package. In some places, however, wooden boxes are used for packing the bark.

The extermination of the tree from many localities by reckless bark-cutting has led to attempts being made to cultivate the tree on a large scale in other parts of the world. The idea of cultivating cinchonas out of their native regions was advanced by RUIZ in 1792, and by FÉE, of Strasbourg, in 1824. In 1838 ROYLE pointed out that suitable areas for the purpose might be found in the Neilgherry Hills, and probably in many other parts of India. The subject was also urged in reference to Java by FRITZE, MIGUEL, and other Dutch botanists and chemists.

The first important attempts at cinchona cultivation were made by the Dutch. HARSKARL collected 400 specimens of plants, which were despatched to Java, and formed the nucleus of the cinchona plantations.

In 1860 CLEMENTS R. MARKHAM and RICHARD SPENCE, at the request of the British Government, transmitted to India a large number of plants and seeds of various species, which they collected with great difficulty, and in face of considerable danger from the hostile attitude of the people and the jealousy of the Bolivian Government.

PRINCIPAL SPECIES OF CINCHONA.

Species.	Native Country.	Where Cultivated.	Product.
Cinchona officinalis,....	Ecuador (Loxa),.....	India, Ceylon, Java,	Loxa or crown bark, pale bark.
" macrocalyx,..	Peru,.....	.....	Ashy crown bark, the sub-species, C. Palton, affords a bark much used in making quinine.
" lanceolata,...	Peru,.....	.....	Carthagena bark; not as good as Palton bark.
" lancifolia,....	New Granada,.....	India,.....	Columbian bark; imported in immense quantities.
" pitayensis,...	New Granada,.....	India,.....	Pitayo bark; very valuable; the chief source of quinidine.
" scrobiculata,.	Peru,.....	.....	Formerly known as red cusco bark.
" peruviana,...	Peru,.....	India,.....	Grey bark, Huanco or Lima bark; chiefly consumed on the Continent.
" nitida,.....	Peru,.....	India,.....	
" micranthra,...	Peru,.....	India,.....	
" calisaya,....	Peru, Bolivia,.....	India, Ceylon, Java, Jamaica, Mexico,.....	Calisaya bark, Bolivian bark, yellow bark.
" succirubra,..	Ecuador,.....	India, Ceylon, Java, Jamaica,	Red bark.
" cordifolia,....	New Granada, Peru,....	.....	Columbian bark (in part).
" tucujensis,...	Venezuela,.....	.....	Maracaibo bark.
" pubescens,...	Ecuador, Bolivia, Peru,..	.....	Arica bark.

Previously to the arrival in India of the first consignment of plants, careful inquiries were instituted from a meteorological and geological point of view as to the localities best adapted for the cultivation. This resulted in the selection, for the first trial, of certain spots among the Neilgherry Hills, on the south-west coast of India, and in the Madras Presidency.

Of this district the chief town is Ootacamund, about 60 miles south of Mysore, and the same distance from the Indian Ocean. Here the first plantation was established in a woody ravine, 7000 feet above the sea level. Other plantations were formed in the same neigbourhood, and so rapid was the propagation that six years later there were more than one and a half millions of cinchona plants in the Neilgherry Hills alone. The species that grows best there is *C. officinalis.*

Plantations have also been made in the coffee-producing districts of Wynaad, and in Coorg, Travancore, and Tinnevelly, in the valleys of the Himalaya, in British Sikkim, in the Kangra valley of the Western Himalaya, in the Bombay Presidency, in British Burmah, and in Ceylon.

The cinchona barks vary considerably in colour and texture. The taste is in all cases bitter and disagreeable, accompanied sometimes with decided astringency. Except in the case of *C. officinalis*, they possess no marked odour.

The barks employed in pharmacy are chiefly of three kinds:—1. *Pale Cinchona Bark*, *Loxa Bark*, *Crown Bark.* This bark was previous to the use of quinine, and for long afterwards, the ordinary Peruvian bark of English medicine; it is only found in the form of quills, which are occasionally as much as a foot in length. The thinnest bark is scarcely stouter than writing paper, the thickest may be one-tenth of an inch. It has a well marked-odour, *sui generis*, and an astringent bitter taste.

2. *Calisaya Bark*, *Yellow Cinchona Bark.*—This bark, the most important of those used for medicine, is imported in quills and also in flat pieces. Its colour is a rusty brown.

This bark is rich in quinine, and contains but a small proportion of other alkaloids. Analyses of this bark from six of the leading varieties gave the following results (C. H. Wood, Quinologist to the Government of Bengal):—

	1.	2.	3.	4.	5.	6.
Total alkaloid,	1·6	6·1	5·57	7·1	5·75	7·4
Alkaloid soluble in ether,	0·82	5·9	5·21	6·93	5·75	7·4
Crystallized sulphate of quinine,	none	4·53	4·6	6·92	5·34	6·2

It is obvious that the bark from the best of these varieties is admirably adapted for the manufacture of sulphate of quinine; but *C. calisaya* grows under more limited conditions than *C. succirubra*, is more difficult to propagate, and has therefore not made the same progress. The Government of Bengal are, however, bestowing much attention on the propagation and extension of good varieties of *C. calisaya.*

3. *Red Cinchona Bark.*—The least important of the barks; though, from the tree yielding it, *C. succirubra*, being a very free grower, it is now being largely cultivated in Bengal.

The total number of trees growing at Sikkim is estimated in round numbers at 2,500,000. The crop of 1875-76 was 211,931 lbs. of dry bark. The proportion of total alkaloid is greatest in the bark of the root, and diminishes towards the branches. The average yield of the plantations contains from 4 to 5 per cent. of total alkaloids, the average composition of which C. H. Wood gives as:—

	Per Cent.
Quinine,	16·31
Cinchonidine,	30·53
Cinchonine,	35·26
Amorphous alkaloid,	17·90
	100·00

The plantations now yield 360,000 lbs. of dry succirubra bark, containing alkaloids in this average proportion.

The Government of India having determined to employ this bark in the preparation of a cheap medicine, experiments on a large scale have been in progress for some years to determine the best and most economical form of febrifuge obtainable from it.

The general nature of the process provisionally adopted is to exhaust the dry bark by successive treatment with dilute hydrochloric acid, and to precipitate the resulting liquor with an excess of sodium hydrate. The precipitated alkaloids are collected on filters, washed, dried, and powdered. This product is then dissolved in a quantity of acid just sufficient to take up the alkaloids, filtered from insoluble colouring matter, and the solution again precipitated. After washing, drying, and grinding, a fine white powder is obtained, which, however, acquires a slight buff tint by keeping. It never agglutinates in any way, even in the trying climate of India. It is freely soluble in weak acids, and is readily taken up by lemon juice. Its cost price is 1*s.* 9*d.* per ounce (C. H. Wood).

The alkaloids of the cinchonas which have been isolated are:—

Quinine,	$C_{20}H_{24}N_2O_2$
Quinidine,	$C_{20}H_{24}N_2O_2$
Conquinine,	$C_{20}H_{24}N_2O_2$
Cinchonine,	$C_{20}H_{24}N_2O$
Cinchonidine,	$C_{20}H_{24}N_2O$
Paytine,	$C_{21}H_{24}N_2O_2$
Quinamine,	$C_{20}H_{26}N_2O_2$

Quinine always occurs together with cinchonine. Yellow bark contains 2 to 3 per cent. of quinine, and 0·2 to 0·3 of cinchonine; while pale bark contains about 0·8 of quinine and 2·0 of cinchonine; and the red bark about 2 per cent. of quinine and 1 of cinchonine.

Quinine was first obtained impure by Gomeg of Lisbon, and by Pfaff, in 1811. Pelletier and Caventon separated it from the other constituents in 1820. Its composition was ascertained by Liebig in 1838. (Fluckiger and Hanbury, *Pharmacographia*, 1874.)

Quinine is one of the more powerful organic

alkalies. It generally appears, when pure, as an amorphous resinous mass of a dull white colour. It may also be obtained as a hydrate in six-sided prismatic crystals, containing six equivalents, or 10·5 per cent. of water, which are lost on fusion.

Quinine has an intensely bitter taste; it is inodorous, and fuses readily. It dissolves sparingly in boiling, and still more sparingly in cold water. It is easily soluble in ether and in alcohol, especially if hot, and is also soluble in the essential and fixed oils.

Ammonia decomposes the salts of quinine in the cold; but on the other hand, at the temperature of ebullition the ammoniacal salts are decomposed. Tartaric, oxalic, and gallic acids, and the infusion of nut-galls, precipitate solutions of its salts. Quinine solutions, if treated with chlorine gas, become yellow, rose-red, violet, and finally deposit a red resinous matter. A solution of the sulphate, saturated first with chlorine and then with ammonia, acquires a grass-green colour, and deposits a green powder. With tincture of iodine, the solution yields a clear brown liquid, which on concentration deposits saffron-coloured scales of a new compound. To detect small quantities of quinine, precipitate the suspected liquid with calcined magnesia, and evaporate to dryness; then extract with 1 part alcohol and 2 parts ether. Evaporate again to dryness, and extract with ether. Now prepare a test liquor, by saturating boiling water with ferricyanide of potassium, to which, whilst hot, add 5 volumes of the strongest chlorine water, and then ammonia, until the blackish-green liquid becomes very alkaline, when the sediment is filtered off. Now mix the fluid to be tested with excess of chlorine water, and drop in the test liquor. A blood-red colour indicates the presence of quinine.

Or, put a minute particle into a watch glass, drench it with 5 or 6 drops of pure sulphuric acid and an equal quantity of water, and add a fragment of bichromate of potash. If quinine is present, the mixture will first assume a green shade resembling that of arseniate of copper, then a beautiful yellow-green, and finally a dark-green. The sulphate, similarly treated, becomes first a nickel-green, next a copper-green, and finally a dirty yellow. The above-mentioned reaction with chlorine and ammonia may also serve for the detection of quinine. Quinine combines with the acids, forming a series of well-defined and persistent salts, of which the sulphate is the most important.

ACID SULPHATE OF QUININE, usually called the *disulphate*, $C_{20}H_{24}N_2O_2,H_2SO_4 + 7$ Aq., crystallizes in small silky tufts, or in fine acicular prisms; it has an exceedingly bitter taste, and when heated becomes phosphorescent. The dry salt is composed of 1 equivalent of quinine, and 1 of sulphuric acid. In the crystalline state it takes up, in addition, 7 equivalents, or 14·4 per cent., of water. It effloresces in dry hot air. It dissolves in 30 parts of water at 212° Fahr., but is very soluble in alcohol, especially with the aid of heat.

Quinine for medical use is generally prepared as basic sulphate $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$.

The ordinary procedure for obtaining quinine is to exhaust the bark with dilute sulphuric acid, boil the extract with milk of lime, and extract the precipitate thus obtained with alcohol, from which, on concentration, the crude alkaloid separates in crystals. These are redissolved in dilute sulphuric acid, and purified by treatment with animal charcoal and recrystallization.

A more perfect though less rapid process is as follows:—Pound the bark coarsely, and let it steep in water to which one-fifth of an ounce of hydrochloric acid has been added for every $2\frac{1}{4}$ pounds of bark employed. Next morning boil the mixture for two hours, and strain. Submit the bark to a second and a third decoction in water containing only half the above proportion of acid. Make, finally, a fourth decoction in pure water, and keep this for the first acid decoction of a fresh quantity of bark. The bark may now be thrown away. Mix the acid liquors, heat, and add carbonate of soda in slight excess, allowing the precipitate which forms to subside. The precipitate is then placed on a linen filter, and left to drain. It is next pressed and dried at a gentle heat. When perfectly dry it is reduced to powder, and treated from five to eight times with alcohol of 86 per cent., at the heat of the water-bath; squeeze the grounds each time, and filter the alcoholic liquors. The alcoholic fluid contains quinine and cinchonine, with colouring matters and some fatty substances. It is next very slightly acidulated with weak sulphuric acid, distilled, and the residue allowed to cool in the distillation apparatus.

A crystalline mass appears, which is drained on a linen cloth, to get rid of the black mother liquor. It is then washed with a little water. Make the crystalline mass, which is still highly coloured, into a paste with warm water; mix this with animal charcoal in powder, and leave the paste till next morning. Mix the paste with a suitable quantity of water and boil, taking care to carry the concentration sufficiently far to obtain crystals upon cooling. For this purpose it is preferable to divide the paste into several portions, and to treat them separately. Filter the liquid boiling. Upon cooling, the sulphate of quinine separates in perfectly white crystals. At the end of forty-eight hours let the mother liquor drain off, place the crystalline mass on some double folds of paper arranged on a hurdle, and carry them to the drying stove, taking care to keep the salt covered, since otherwise it would turn yellow. As soon as dry the salt must be removed from the stove, or it will effloresce and lose weight. The mother liquor which had deposited the white sulphate is next precipitated with ammonia, which throws down all the quinine and cinchonine still contained in it. Dissolve the precipitate with the aid of heat, in water acidulated with sulphuric acid, and add, towards the end of the operation, animal charcoal, and if necessary a little chalk to saturate the excess of acid. Evaporate the liquid to a proper degree of concentration, and filter boiling. A fresh crop of white crystals will be deposited from the filtrate.

Treat the mother liquor of this second operation

in the same way, and continue to proceed in this manner until the whole of the alkaloid is converted into crystallized sulphate. After the third precipitation it is sometimes advantageous to treat the precipitate with alcohol of 64 per cent., which dissolves the quinine alone, instead of dissolving it in water acidulated with weak sulphuric acid. A part of the alkaloid still remaining in the mother liquor is deposited spontaneously as sulphate, in course of time, and may be purified by the usual method.

To extract the quinine still remaining in the mother liquor, the following process has been proposed by GUIBOURT:—Add to the black mother liquor an equal weight of a solution of chloride of sodium of 15° Beaumé. Boil for ten minutes, decant, and submit the brown deposit which has been formed twice more to the same operation. Pour the decanted liquors together, cool and filter, and precipitate the filtrate with ammonia. Redissolve the brown deposit which had separated from the saline liquid in the third operation in water, and add gradually, and in small portions at a time, ammoniated salt-water, taking care to stop short of complete saturation. Filter the liquid off the soft brown precipitate which forms, throw the latter away, and precipitate the filtrate with ammonia. Treat the several ammoniacal precipitates with alcohol. The solution, treated in the usual way, will now yield basic sulphate of quinine.

The quantities of sulphate of quinine furnished by the varieties of bark which occur in commerce are:—2 lbs. 8 ozs. of yellow, or Calisaya bark, without rind, yield 490 to 530 grains sulphate of quinine; the same quantity, with the rind, yields 360 grains: 2 lbs. 8 ozs. of the red bark, *C. oblongifolia*, will yield 248 grains sulphate of quinine, besides about half that quantity of sulphate of cinchonine: 2 lbs. 8 ozs. of pale bark should yield 180 grains sulphate of quinine, and 124 grains of sulphate of cinchonine.

Herring's Process.—The powdered bark is boiled in a solution of caustic soda, pressed, returned to the boiling tub, agitated with cold water, again pressed, and if much colour passes from the second washing the bark is returned to the tub, washed again with cold water, and pressed once more. The treatment of the liquors obtained by the soda boilings and washings is described under the second operation. The bark is now boiled with dilute sulphuric acid, kept in constant agitation by proper machinery, and this first boiling is run into the evaporating pan, a large water bath kept by steam pipes at a temperature of 120° Fahr., and agitated by paddles. The bark is again boiled with sulphuric acid and water as above, and the liquid run into the evaporating pan. The third, fourth, and fifth boilings are not evaporated, but reserved to extract the next portion of bleached bark that is brought forward. When the liquor from the first two boilings is sufficiently concentrated, it is allowed to cool, and filtered. Thus the flocculent colouring matter is separated, and the acid solution is now fit for precipitation. The filtered cold solution is treated by caustic soda, and the precipitated quinine is drained, washed, and pressed. It is now treated with dilute sulphuric acid, and crystallized into a very thick paste. When cold these crystals are pressed, washed, and again pressed. This removes the colouring matter and the chief part of the sulphate of cinchonine. The pressed cakes of sulphate are finally dissolved in a large quantity of water and recrystallized. The crystals thus obtained form the hospital sulphate of quinine. The liquid which drains away from the second crystallization removes the small quantity of cinchonine which may not have been got rid of by the first crystallization. If the sulphate is required perfectly white it is redissolved, treated with animal charcoal, and again crystallized.

The blood-red soda-boilings of the bark mentioned in the first operation are treated with hydrochloric acid, in order to retain in solution the alkaloids which have been extracted by the alkaline boilings. The ordinary view that quinine is insoluble in alkalies is pronounced by HERRING erroneous. He states that, in acting upon large quantities of bark, the amount retained in solution is very considerable. The caustic alkalies exert less solvent power than the carbonates, and caustic soda least of all. After the red alkaline liquor has been acidulated with hydrochloric acid, it is concentrated and precipitated with lime. The precipitate, a mixture of quinine and lime, is washed, dried, and powdered, and finally extracted with hot alcohol. On distilling off the alcohol, the crude alkaloids are left behind. These are then treated with dilute sulphuric acid, exactly as in the former process, a larger quantity of water being required for removing the colouring matter and the sulphate of cinchonine. After two more crystallizations the sulphate is obtained perfectly pure.

The first operation yields from 80 to 90 per cent., and the second from 10 to 20 per cent. of the required product.

RESINS.—See VARNISH.

SALT.—*Sodium Chloride; Chlorure de Sodium*, French; *Koch Salz*, German. Symbol, NaCl.—This substance is an essential constituent of food, and is besides consumed in enormous quantities in manufacturing operations.

Sodium chloride occurs in every part of the human frame; it is organized in the solids and dissolved in the fluids. In England and the United States the quantity of salt consumed gives 20 lbs. per annum to each person; in France the average is about 15 lbs.

Sodium chloride crystallizes in cubes, which are often grouped into pyramids of steps; or the reverse of this, a pyramid of steps having its apex downwards, may be produced. It is only slightly more soluble in hot than in cold water—

100 parts of water at		0° C.,	dissolve	35·82	per cent.	NaCl.
"	"	14° C.,	"	35·87	"	"
"	"	100° C.,	"	36·61	"	"
"	"	110° C.,	"	40·35	"	"

Salt decrepitates when suddenly heated, owing to a small quantity of water being inclosed between the plates of the crystals. It melts at a low red heat, and may be volatilized in a hot furnace; its specific gravity is 2·557. It deliquesces in moist air.

Two varieties of salts are in use in commerce—rock salt, and the salt produced by the purification and evaporation of salt brines.

Rock Salt.—The deposits of rock salt which occur in the earth's crust, and the brine springs which at various places rise to its surface, appear to be confined to no particular series of strata, but to be distributed somewhat indiscriminately. Thus, the inexhaustible mines of Wielitzka in Galicia, the deposits at the base of the Carpathian mountains, as well as in many other parts of Central Europe, are found in the Tertiary: in some parts of Germany, again, salt is obtained from strata equivalent to our New Red Sandstone; in the Austrian Alps an impure deposit, mixed with clay and gypsum, occurs in Oolitic Limestone; whilst in many countries, and even in England, salt springs burst out of the Carboniferous and older rocks.

The great English deposits, however, exist in the upper members of the New Red Sandstone, in the green and red marls of that system, which has occasioned the application of the term "saliferous" to the whole series of rocks of which it is composed; a term shown by Murchison to be incorrect, inasmuch as the middle and lower members of that group are destitute both of rock salt and saline waters.

The salt-producing strata of the New Red Sandstone lie both in Cheshire and Worcestershire in a basin of Lias: at Northwich, in Cheshire, masses of rock salt exist 60 feet in thickness, 1400 yards in breadth, and a mile and a half long; and from a bed still lower, salt has been removed to a depth much exceeding double this. In Worcestershire the deposits, although large, do not appear to be on so gigantic a scale. The whole depth of the rocks constituting the matrix has been estimated at upwards of 600 feet, and the layers of salt in the sinkings at Stoke Prior vary from mere veins to deposits of more than 30 feet in thickness.

The Cheshire salt beds furnish most of the salt used in England. The broad valley extending from near Malpas to Congleton (sweeping in the form of a crescent between the Red Sandstone hills of Shropshire and the Staffordshire coal-field on the one side, and the high ground of the Peckforton hills and Delamere range on the other), appears to be occupied by the saliferous and gypsiferous beds, lying as it were in a trough, to which the adjoining portions of both the above ranges dip. There are several faults and dislocations in this field; thus, at Lawton, rock salt is found 290 feet above the sea level, while at Winsford it occurs 90 feet below, and at Frodsham Bridge no salt was found at 450 feet below the sea level.

The rock salt lies in two beds principally. The depth to the first bed at Northwich varies with the undulations of the land, and also slightly with the irregularity of the bed itself, from 96 to 159 feet. At Winsford the depth is 189 feet. The thickness of the upper bed varies at Northwich from 84 to 90 feet in the pits sunk to the north-west, decreasing near the east border to 81 feet. It thins off towards the south-west, losing 15 feet in thickness in the course of a mile. Below this lies a bed of indurated clay, 30 feet in thickness, and containing several thin veins of salt, and this overlies the second or great bed. At a pit at Marston, to the north of Northwich, this has been ascertained to be 96 feet thick. At Winsford, however, it is 225 feet thick. At Northwich the first 60 to 75 feet of rock are impure, the salt being contaminated with much clay and bituminous matter; in the next 12 or 15 feet the salt is much clearer, and this portion only is worked. The clear portion corresponding to this is worked at Winsford at a depth of 210 feet in the rock.

The mining operations concerned in the getting of rock salt hardly require any description. A shaft like that of a coal pit is sunk to such a depth as the position of the rock necessitates, and galleries are worked out from this. The rock is broken down by blasting, beginning at the top of the working and proceeding downwards.

The rock salt was formerly dissolved and purified; but at present brines of great purity and strength, and in unlimited quantity, may be obtained at so little cost that recourse is seldom had to the rock salt. There is therefore little use for it, and most of the rock mined is exported.

Salt Springs and Wells.—*Brines.*—A fresh-water spring passing over a bed of rock salt, becomes impregnated with that substance, and there results a salt spring or well.

ANALYSES OF SALT BRINES.

The numbers refer to 100 parts by weight of water.

	Moutiers.	Schonebeck.	Friedrichshall.	Clemenshall.	Hall.	Sulz.	Durrenburg.	Rodenberg.	Artern.	Nauheim.	Kreuznach.	Salzhausen.
Sodium chloride, ...	1·058	9·623	25·5625	25·9021	25·7180	23·4733	6·599	5·173	2·829	2·3600	1·415	0·943
Potassium chloride, ...	—	0·007	—	—	—	—	0·008	—	0·004	0·0524	0·006	0·009
Magnesium chloride, ...	0·030	0·083	0·0059	—	—	—	0·092	0·166	0·038	0·0339	0·023	0·080
Calcium chloride, ...	—	—	—	—	—	—	—	—	—	0·1935	0·261	—
Potassium sulphate, ...	—	0·014	—	—	—	—	0·004	—	0·004	—	—	—
Calcium sulphate, ...	0·251	0·339	0·4374	0·4445	0·1705	0·5080	0·250	0·515	0·158	0·0052	—	0·080
Sodium sulphate, ...	0·100	0·249	—	0·0197	0·0289	—	0·208	—	0·092	—	—	—
Magnesium sulphate, ...	0·055	0·012	0·0221	—	—	—	0·004	0·005	0·004	—	—	—
Calcium carbonate, ...	0·076	0·026	0·0100	0·0195	0·0037	0·0162	0·026	0·010	0·042	0·2133	0·003	0·057
Magnesium carbonate, ...	—	—	—	—	—	—	—	—	—	—	0·001	—
Ferrous carbonate, ...	0·012	0·001	—	—	—	—	0·004	—	0·012	—	0·005	0·001
Silicic acid, ...	—	—	—	—	—	—	—	—	—	0·0021	0·013	0·001
Organic matter, ...	0·001	—	—	—	—	—	0·012	—	0·017	—	—	—
Total, ...	1·593	10·354	26·0379	26·3859	25·9211	23·9975	7·207	5·869	3·190	2·8604	1·727	1·171

Salt wells are also made artificially by pumping water into excavated salt mines.

When the brines are very weak, they are always made to undergo a preliminary evaporation in the air; and when the presence of sulphates and the chlorides of calcium and magnesium are calculated by their quantity to impair the commercial character of the product, certain purifying processes are had recourse to by which these are removed. When ferrous carbonate is present in the weak brine, it is generally got rid of by exposing the brine for some time to the air. The process of evaporation with weak brines is carried on in France and Germany in what are termed graduating houses. These are large wooden structures, from 800 to upwards of 5000 feet long by about 40 feet broad, covered over at the top, and open at the sides to allow a free circulation of air through the interior. The roof covers and protects from the rain several very large but shallow wooden cisterns intended to receive the brine, or there may be only one cistern, divided by wooden partitions into several separate compartments; but the extent of these divisions, their collection under one roof, or their separation, are determined by circumstances purely local, such as the character of the water, or indeed the motive power available in distributing it. The several compartments are used to contain the brine in different stages of concentration. The first is intended to receive the brine itself; the second to receive the same after it has been concentrated by exposure to the air in minute streams, &c. The position of these graduating houses is such that they shall be exposed in the direction of their greatest length to the prevailing winds.

Various arrangements have been devised to increase the evaporating surface of the brine; but that which now supersedes all others consists in pumping the liquor up to the summit of a high reservoir, and allowing it to trickle through the interstices of bundles of thorn built up in the form of a wall, and supported by woodwork.

On the thorn sticks a scale gradually deposits, consisting of calcium oxide, calcium and magnesium carbonates, and calcium sulphate, and forming what is called *thornstone*. This incrustation at length attains such a thickness as to fill up the interstices between the sticks. The stack has then to be taken down, and the thorns renewed. This happens about every five or eight years, according to the character of the brine.

The rapidity with which water is evaporated by the use of thorn stacks is remarkable. Thus at Schönebeck the thorn surface is 390,000 square feet, and under very favourable circumstances evaporates 3·7 cubic feet during the twenty-four hours from each square foot. And from very careful experiments by Berthier, at his works at Moutiers, it appears that 13 gallons of water are evaporated under ordinary circumstances every twenty-four hours from each square foot of thorn wall. It is a remarkable fact that the water evaporated from the thorn surface is practically proportional to the surface exposed, whatever be the density of the brine.

When the brine in the tanks under the thorn stacks has been brought to a specific gravity of between 1·14 and 1·16, it is run out into large settling reservoirs with just sufficient lime to decompose the magnesium chloride. These reservoirs are of immense capacity; for the evaporation in the air taking place only during the summer months, the reservoirs have to be made large enough to hold a great quantity of the concentrated liquor to be evaporated during the winter months. The eight reservoirs at Salza have a capacity of nearly 3,000,000 cubic feet. In these reservoirs the brine deposits all suspended matters, and the clear liquor is then run into wrought-iron tanks to be evaporated to saturation.

The pans used are from about 60 to 80 feet long, by from 20 to 40 feet broad, and 2 feet deep, and are made of thin sheets of wrought iron rivetted together. Each pan is heated by two or even four fires, and the flues are so built that the heat shall be as evenly distributed over the whole bottom of the pan as the brick supports upon which it rests will allow.

The pans being three parts filled with brine, and a little blood or grease added, are brought as rapidly as possible to the boiling point. A scum now forms on the surface, which is skimmed off. This scum consists of the organic matter in the brine, and a little bitumen, which is found in all brines from natural springs. In the meanwhile the brine, which is saturated with sulphate of lime, gradually deposits this on the bottom of the pan. When about one-fourth of the original brine has been evaporated, new brine of specific gravity 1·16 is again pumped in, and the process of boiling and removing the scum is continued until the brine in the pan has been brought almost to the point of saturation; it is then run into other pans of a similar shape and about equal capacity, to be evaporated to dryness.

The deposit on the bottom of the pan gradually attains a thickness calculated to interfere very materially with the conducting power of the iron, and so occasions much loss of heat; the pan has then to be scaled. Of course the necessity for performing this operation will vary considerably with the degree of purity of the salt. It is usual, however, to scale the pan after it has been filled up from eight to about fifteen times.

The deposit consists of sulphate of lime and sulphate of soda, inclosing mechanically a quantity of common salt.

Boiling down is performed in wrought-iron pans, similar to those described above. They inclose an area of about 400 square feet. The bottom of the pan inclines a little towards the centre. Over the pan is a dome-shaped structure of wood, terminating in a kind of chimney, for the purpose of carrying away the vapour. The woodwork supporting the dome is open at the side, immediately over the pan, that there may be a free circulation of air over the surface of the brine. During the beginning of the boiling down the pans are briskly heated; towards the end, when much salt becomes deposited on the

bottom, the fires are slackened, that the bottom of the pan may not be burned.

The process is continuous, the salt being taken out as it falls by means of scoops, perforated at the bottom to allow the mother liquor to percolate.

In the case of lime having been added in the settling pan, or at the beginning of the concentration, the mother liquors do not become too impure to be evaporated down to dryness in the boiling-down pan, even after the pan has been filled up with new brine several times. There is also an additional advantage experienced at this stage of the manufacture, from lime having been added to throw down magnesia, inasmuch as otherwise, during the process of evaporation, chloride of magnesium forms a crust on the surface of the liquid, which re-forms almost as soon as broken, thereby preventing very materially the escape of vapour. The formation of this crust, however, may be avoided equally well by the addition of a little sulphate of soda.

The salt having been removed from the crystallizing pans by the strainers, is collected into large heaps on a perforated floor to drain further; it is then transferred to the "drying chamber." This is simply a long chamber, heated by the flues from the fires used to evaporate the brine. These flues converge into one or two main flues, which are made to pass along the bottom of this chamber. The salt is either packed up in shallow wicker baskets, or it is put into moulds, and these are piled up above the flue in the drying chamber, and there allowed to remain until the salt no longer loses much moisture, when it is fit for the market.

In England, all the salt prepared is obtained from the evaporation of strong brines by artificial heat. The brines used are saturated, or nearly saturated solutions of salt in water, and contain from 23 to 26·5 per cent. of pure chloride of sodium, besides other constituents; while a saturated solution of salt in water only contains 27 per cent. of salt. Indeed, several experiments tend to show that some brine springs would seem to hold in solution more chloride than would be taken up by the same amount of water, however long it were left in contact with dry salt.

The brine springs of Cheshire do not rise to the surface of the ground. They emerge from the surface of the rock; and when the spring is tapped, will rise in the bore hole from 80 to 90 feet. In the neighbourhood of Winsford and Northwich, a shaft is sunk in the ground 6 feet square, and about 180 feet deep. The sides of the shaft are carefully boarded with planks, and an inner planking of 6-inch boards, 4 feet square, is then built in, and the space between the boards well puddled with clay, to keep out any surface springs of fresh water. The inner boarding is firmly built in, and made more secure by cross-stays of stout wood. An iron pipe about 9 inches internal diameter is then let down into the boring. The brine will rise in this pipe about 90 feet; it has consequently to be lifted by a pump to about the same extent. A continuation of the pipe from the pump conducts the brine into a large reservoir lined with masonry. This reservoir, which may be about 200 feet long by about 60 or 80 broad, and perhaps 6 feet deep, is not built for the purpose of allowing sedimentary matter to deposit, for the brine as it is pumped up is perfectly clear and free from particles in suspension. It is of a clear sea-green colour, and the reservoirs are built to serve merely as a store of brine on a high level, from which it may be drawn down to supply the evaporating pans as needed.

The evaporating pans are contained in a shed which may be 400 feet long by about 80 feet broad, and about 30 feet high, open at the sides to permit a free current of air to pass over their surface. The pans are set in a firm foundation of brickwork, which does not, however, extend up the sides. There are generally four furnaces to each pan, and the flues, so built as to support the pan, radiate over the whole of the bottom. There are usually three pans in a series, under two of which, furthest removed from each other, are the fire-places. The flues passing under these are continued under the third, and meet in the centre, at which point they unite into one, and the flue is connected with the chimney; but in order to economize as much as possible the heat of the flue, a chamber is built over it in its course to the chimney, and this is made use of as a drying stove for the squares of salt.

The Cheshire brines, which are of specific gravity 1·200, and contain about 24 per cent. of common salt, are of so pure a quality that they require no preliminary concentration. The brine is, therefore, at once run into the evaporating pans, which are of sizes varying with the source of heat, and evaporated by the direct action of the fire, or by the waste heat of the steam engine used to pump up the brine.

Those pans in which the salt is evaporated by a boiling heat are about 20 feet square and 18 inches deep. Those where a lower temperature is used are about 40 feet long by 20 broad, and 2 feet deep. The pans are made of $\frac{1}{4}$-inch iron boiler-plates rivetted together. They incline somewhat towards the end furthest removed from the fires, that more salt may be deposited on that part. The inclination is from 6 to 8 inches in the whole length.

Three kinds of salt are manufactured in Cheshire; the difference, however, consists in the size of the crystal, depending upon the rapidity with which the evaporation is conducted. Thus the finest-grained salt is made by rapid boiling; the coarsest at a temperature of about 150° Fahr.; and the medium quality between these two points.

The evaporating processes are conducted as follows:—Brine is run into a pan until it is three parts full; a little glue, and sometimes a little waste grease, is then thrown in to assist in the formation of a scum, and partly to prevent the crystals of salt as they fall from adhering to the bottom of the pan. The brine is then brought to the boil as rapidly as possible, and a scum which forms on the top is removed by lightly skimming the surface with a piece of board. The crystals of salt begin to separate almost as soon as the brine is brought to the seething point, and when about half the water has been

evaporated fresh brine is run in. The salt that has boiled out is removed twice in the twenty-four hours. This operation is effected by a perforated scoop, and the salt is put into wooden moulds, or tubs, about 18 inches high and 9 inches broad at the top, and diminishing to about 7 inches at the bottom. These tubs are put into the salt pan to be filled, and stand on a ledge on the side about 6 inches from the bottom of the pan. When the tubs are filled the salt is slightly pressed down, and the tubs are removed from the ledge on to a perforated floor, so that the mother liquor may drain away from the salt. To allow of this there are two slits in the bottom of the tub. When the salt in the tubs has drained twelve hours, the tubs are reversed, and then withdrawn from the squares of salt, which are removed to the drying chamber, where they are allowed to remain until they become dry. From a salt-pan 20 feet square 200 tubs of salt, each containing 30 lbs. of dry salt, are removed in a day. The pans are not allowed to cool, except for purposes of cleansing, the brine being repeatedly pumped in, and the process of evaporation being continuous. About once a week the salt is more thoroughly removed than usual, and the brine in the pan allowed to run low; the pan is then scaled over the fireplace. This operation is performed with a pickaxe furnished with a long handle, and having the iron flukes flattened at the ends. A man stands on the floor that runs round the pan, and by striking with the axe he loosens the incrustation, and then removes it with a rake and spade. The scale consists of a little clay and sulphate of lime, but principally of common salt which has been burnt on to the bottom of the pan. When a pan has been worked for a month, a scale will have gradually formed over the entire bottom. The whole of the salt is then removed, the fires put out, and the mother liquors, being of little value where there is such abundance of brine, are run away. The whole underpart of the pan is then scaled with a hammer and chisel.

The brine springs of Droitwich, Worcestershire, are stated by Sir C. Hastings to have been in use in the time of the Romans. At both Stoke Prior and Droitwich a shaft of considerable diameter is sunk, and lined with an iron casing to prevent inflow of fresh water. In this the pumps which remove the brine and convey it to the reservoirs are fitted, and from the bottom of this upper tube a narrower pipe is carried down to a considerable depth, until, in fact, it reaches the subterranean brine chamber. The depth of the iron casing at Droitwich is 150 feet, that of the boring below 25 feet; and so abundant is the supply of brine, that if the pumps cease working, the shaft is speedily filled to within 9 feet of the surface. At Stoke the supply appears now to be equally inexhaustible, although in former years it failed; but the present proprietor (J. Corbett) has bored deeper than his predecessors, and has, by means of a shaft 225 feet deep, and a boring of 348 feet more, succeeded in breaking through the drier and more superficial deposits, and has penetrated a large and probably inexhaustible reservoir.

The brine, thus pumped out of the pits as fast as it is supplied, is treated at both places in a precisely similar manner; it is conveyed by pipes directly from the pumps into large but shallow reservoirs, which act as feeders to the numerous pans in which the evaporation is carried on. The pans vary in length from 60 to 100 feet, and are about 20 feet broad and 18 inches deep; the evaporation is conducted as already described. In the large pans, such is the difference of temperature in different parts of the pan, from the furnace being placed at one end, that while the fine-grained salt is produced at the hottest end, bay salt is the result of the diminished temperature at the other. The salt as it crystallizes out sinks to the bottom, and is continually removed by the workmen, who place it in tall boxes having their bottoms pierced; in these the salt is allowed to drain for a time, after which the moulds are taken to the drying house, as already described.

At J. Corbett's works circular pans with closed covers are used for concentrating. These are charged and heated in the same manner as the ordinary pans; but the steam from them is carried by means of pipes through the furnace, and after being superheated it passes through a supplementary series of open pans, where it keeps the brine at boiling point. The pans, which are 24 feet in diameter, are fitted with circular rakes, worked by machinery in the same manner as the stirrer of a mash-tun. By this means the crystals are precipitated in very small particles, and a very white fine-grained salt is the result. The process is a continuous one, and the salt is drawn from an aperture into a long trough, which is attended by a number of boys, who fill the squares and pass them to the drying-room. The general advantages of this process are, the saving of time by the continuous operation, the double utilization of both the fire heat and the steam, and, consequently, great economy of fuel, and a larger yield of salt.

The following analyses of the brines thus heated were made by A. B. Northcote:—

	Droitwich Brine.		Stoke Brine.
	January.	August.	August.
Sodium chloride,	23·2932	22·4521	25·4923
Sodium bromide,	trace.	trace.	trace.
Potassium sulphate,	—	trace.	trace.
Sodium sulphate,	·3712	·3905	·5948
Calcium sulphate,	·3690	·3878	·2612
Sodium carbonate,	·1382	·1157	·0161
Magnesium carbonate,	·0420	·0343	·0347
Calcium phosphate,	—	trace.	trace.
Ferric phosphate,	—	trace.	trace.
Silica,	trace.	trace.	trace.
	24·2136	23·3804	29·3991
Solid residue by direct evaporation,	24·2064	23·4205	26·4749

Salt from Sea Water.—In Sweden, Russia, and other northern countries, salt is sometimes obtained by freezing the sea water in large reservoirs. This process depends on the fact that when sea water

freezes, the ice formed consists of pure water; the mother liquor therefore, by repeated congelation, becomes more and more impregnated with salt, and can be profitably boiled down. The salt obtained is far from pure; it would be much improved if lime water were added in sufficient quantity to remove the sulphuric acid as calcium sulphate, and to decompose the chlorides. The following analyses of salt from foreign sea water are by HESS:—

	Irkoutsk.	Selenguisk.	Oustkoutsk.	Okhotsk.		
				1st Soccage.	2nd Soccage.	3rd Soccage.
Sodium chloride,	91·5	74·7	76·3	86·0	77·6	79·1
Aluminium "	2·6	6·5	1·2	3·6	6·2	7·8
Calcium "	1·1	1·4	3·8	0·9	0·9	0·7
Magnesium "	2·0	3·6	3·6	2·0	1·7	0·8
Sodium sulphate,	2·8	13·8	12·6	7·5	13·6	11·6
Calcium "	—	—	2·5	—	—	—
	100·0	100·0	100·0	100·0	100·0	100·0

In the south of Europe the evaporation is effected by exposing the sea water in thin layers to the influence of the sun and air. The sea at the rising of the tide is allowed to run through sluice gates into a pond, covering about an acre of ground, and about 6 feet deep. The gates are then closed, and the water gradually deposits all the matter in suspension. From this reservoir the clear water is conducted by pipes into a series of shallow basins, the whole covering some acres of ground, where, by exposing a very large surface to the drying influence of the sun and air, it rapidly evaporates. These basins are so arranged that the water shall flow slowly from the first reservoir downwards through the whole series. In favourable weather the sea water becomes brine in about seven days. It is then pumped into iron pans, and boiled for twelve hours, during which time it is skimmed to remove impurities. The crystals of salt then begin to appear, are shovelled out into wooden troughs, with holes at the bottom to allow the "bitters" (*i.e.*, the mother liquor, containing the magnesium salts, &c.) to run off.

In the salt gardens on the Mediterranean the whole process is conducted by aerial evaporation, the concentrated brine being run into crystallizing ponds, whence the salt is fished out, and drained upon sloping beds, termed salt tables. The mother liquors run back into the sea, and the salt is exposed to the air for a short time, so that by absorbing moisture the more deliquescent salts may be removed.

SILVER.—French, *Argent;* German, *Silber;* Latin, *Argentum.* Symbol, Ag. Atomic weight, 108.

Specific gravity varies from 10·5 to 10·62, according to the condition in which it exists. Equivalent, 107·928 (MARIGNAC); 107·929 (STAS); melting point, 1832° Fahr. (1000° C.) (POUILLET); 1893° Fahr. (1034°C.) (GUYTON-MORVEAU); 1904° Fahr. (1040°C.) (RIEMSDIJK). Specific heat, 0·05701 (REGNAULT); 0·05507 (DULONG and PETIT). Heat-conducting power, 100; electric-conducting power, 100 (at 32° Fahr.); both decrease as the temperature rises.

Silver possesses a characteristic pure white colour, and is capable of taking a more perfect polish than any other metal in a pure state; it is, however, inferior in this respect to steel. It is found native, and also in the mineral form in combination with various non-metallic elements, such as sulphur, chlorine, &c. As already mentioned in the article on GOLD, that metal is always found alloyed with silver, though sometimes only in minute quantities. The hardness of silver is considerably increased by the addition of a small quantity of copper; but when in a pure state it is intermediate in this respect between this metal and gold.

Historical Notice.—The discovery of silver appears to have been coeval with that of gold, and dates back to the earliest times of the world's history. In the Book of Genesis we learn that silver, by weight, was "current money with the merchants" about 2000 years before the Christian era, and frequent mention is made of this metal in the subsequent books of the Bible.

The principal sources from which the ancients obtained their gold have been mentioned in the article on that metal, and probably much of their silver was obtained from the same localities. PLINY speaks of a people named the Dardaneans, who inhabited a country the richest of all India in gold mines; and the Selians, he says, have the most abundant mines of silver. According to XENOPHON, the Athenians worked the silver mines of their own country—Attica—from an unknown age, as well as the gold mines in their foreign possessions in Thrace, and in the island of Thasos. Epirus also had silver mines, which continued to be worked in the time of STRABO.

But the country most productive of the precious metals, and especially of silver, in very remote ages, was the Spanish peninsula. Gold, iron, and lead were procured in the south, and some tin in the north of Spain; but the gold was probably of small amount, and the chief mineral wealth of the country was in silver.

During several centuries which succeeded the overthrow of the Roman Empire, mining operations appear to have been suspended throughout Europe, and the dates at which they were generally resumed are not certainly known. The chief sources of the precious metals in the middle ages were the Austrian mines; and of these, it is considered probable that the mines of Chemnitz and Kremnitz in Hungary were the first worked. FERBER dates the opening of Chemnitz in 745, and that of Kremnitz in 770; but AGRICOLA, who states that they had previously been worked by the Romans, dates their reopening nearly a century earlier.

Sources.—The two chief argentiferous minerals in Hungary are sulphide of silver and argentiferous galena, while the mountains in which the mines occur consist for the most part of trachytes, associated with porphyry and syenite. From 2 to 20 ozs. of silver are contained in 100 lbs. of the argentiferous lead, and the present annual produce of Hungary, Transylvania, and the Banat is about 92,000 lbs. troy; but this is a considerably less

amount than was produced about a century ago. In Bohemia celebrated mines exist at Joachimsthal, on the southern slope of the range of mountains known as the Erz Gebirge; but they are now almost exhausted, whereas those at Freiberg, to the north of this range, in Saxony, still produce very large annual supplies of the precious metal.

It is interesting to note that the productiveness of the mines has *increased* with the depth; for notwithstanding the greater cost of working, the produce has, as a rule, increased annually. Formerly many of the mines were profitably worked in Saxony; but since the Thirty Years' War their yield has been comparatively small, the total annual produce of this country being about 80,000 lbs., of which Freiberg alone produces 78,000 lbs. Silver mines are said to have been worked by the Romans in the Tyrol, and during the middle ages important mining operations were carried on in this locality. The average annual yield during last century was about 6000 lbs, but the amount produced now is unimportant.

The most productive of the mines in the Hartz district at the present day are in the neighbourhood of Andreasberg, some of which are worked to a depth of over 400 English fathoms. The district of Clausthal also yields considerable supplies of argentiferous galena; and according to PHILLIPS, the average annual produce of the Hartz mines is about 27,540 lbs. troy.

Since the rich mines of Spain were last worked by the Romans, they seem to have been greatly neglected. CARDENNE, however, asserts that the mines of gold and silver which existed in that country were a great source of wealth to the Arabs. The mine of Zalamea, to the south of the river Guadiana, in Andalusia, appears to have been worked in the middle ages.

In 1839 the celebrated mines of the Sierra Almagrera, in the province of Almeria, were discovered; and in 1843 those of Hiendelaencina, in the province of Guadalajara. These latter, which are considered the most important silver mines of Spain, are situated about 70 miles north of Madrid, and were discovered by a returned Mexican miner, who observed a resemblance between some rock and the ore which he had worked in the New World. The average annual produce of the mines of this district during the twenty years ending 1866 was about 32,390 lbs. troy, about 90 ozs. of fine silver being generally obtained from each ton of ore. The method invented by PATTINSON for desilverizing lead —a process fully explained in the article LEAD— has been very generally introduced in the provinces of Murcia and Almeria, as by its means silver may be profitably extracted from slightly argentiferous lead.

The silver mines of Norway and Sweden were long famous, but have latterly become less productive. The mine of Sabl, or Sala, is said to have been worked five hundred years ago. The silver mines of Kongsberg, in Norway, were discovered in 1623, and have been worked almost uninterruptedly up to the present day, yielding a large profit. The annual produce, however, is very irregular, and has during the last few years been about 8000 lbs. troy. They are now worked at a depth of about 300 fathoms, the silver occurring in parallel belts of rock of considerable extent, impregnated with sulphides of iron, copper, zinc, &c.

In Great Britain silver is found in considerable quantities, but always associated with lead in galena, and the amount of the precious metal per ton varies considerably in different parts of the country. That obtained in the Isle of Man is the richest, containing from 50 to 60 ozs. per ton; while in the north of England usually only 1½ oz. are obtained from each ton of ore. The average annual produce obtained by this means in the United Kingdom is about 620,000 ozs.

In several districts of France argentiferous galena is produced in large quantities: the principal of these are Pontgibaud in Puy-de-Dôme, Poullaouen and Huelgoët in Finisterre, &c. To the former of these special reference will be made when treating of the methods of smelting silver ores. The amount of silver produced by Australia is insignificant.

But, as in the case of gold, the amount of silver obtained in the mines of the Old World is trifling when compared with that produced by the New World; and North, Central, and South America all yield large quantities of the precious metal.

The earliest discoveries were made in Mexico shortly after its invasion by CORTEZ i . 1519, and according to HUMBOLDT, during the years 1785–89, amounted to more than 7,000,000 lbs. troy. Subsequently to this period, however, the produce fell off until 1850, since which time they have produced about 1,000,000 lbs. troy annually. Mining operations are principally conducted in the districts of Zacatecas, Guanaxuato, Fresnillo, and Real del Monte.

The State of Nevada first became known as a silver-producing district in 1859, but the amount since obtained has been extraordinary; and according to PHILLIPS, the mines on the great Comstock Vein, in the range of the Washoe Mountains and near Virginia City, have since that date produced bullion to the value of £25,000,000 sterling, one-third of which was gold. Valuable mines also exist at White Pine, in the Austin district, and in other parts of the state.

The first actual discovery of the precious metal in Nevada appears to have been made in 1857 by two brothers named GROSH; but they died very shortly afterwards, and before their discovery became generally known. Rich deposits were found in 1859 by two Irish miners, and the ground was subsequently purchased by COMSTOCK, whose name was thus given to the entire lode. It was not, however, worked on an extensive scale till the latter end of 1862, and during the five subsequent years it yielded an annual average produce of the value of nearly £3,000,000 sterling. The principal ores found are stephanite and argentite; native, ruby, and horn silver are also found, and polybasite, accompanied by rich argentiferous galena. The rocks inclosing these vary considerably in different

localities. Propylite or compact porphyry invariably exists on the eastern side of the vein (which travels north and south), while on the western face syenite is at times found; the main boundary being a continuous clay selvage or flucan. The occurrence of silver in this vein is thus summarized by Richthofen:—

1. The ore is, in the northern part of the vein, concentrated in chimneys dipping to the south; in the southern part it forms continuous sheets of great length, but which are comparatively narrow.

2. These deposits of ore are inclosed in the eastern and sometimes also in the middle portions of the vein; the western branches are either poor or barren.

3. The richest and largest deposits have been found at those places where the outcrops, including those of the western branches, were most prominent.

4. In the northern part, the vein is at the levels explored invariably poor where it passes a ravine; but in the southern part, the ore continues in the ravines.

5. The richest portions of the lode are south of each ravine crossed by the vein.

6. All the chimneys in the northern part are at those places where the walls, after close contact, rapidly diverge, and cause the vein to expand.

7. All the principal accumulations of ore are at those places where there was most room in the fissure for the deposition of quartz; and they are therefore generally rare where an unusual number of 'horses' obstruct the vein.

The Reese River mining region is an extensive district in the north-eastern portion of Nevada, and covers an area of about 75,000 square miles; it yields nearly all the valuable metals, such as gold, silver, copper, lead, iron, &c.; but only the two former are at present worked to any great extent. The ores at Austin, in about the centre of this region, are chiefly pyrargyrite, or dark red silver ore, while chloride is found in large quantities in the White Pine district. In Idaho, pyrargyrite is found massive, as well as auriferous carbonate and sulphide of lead. The latter is also the principal ore found in Colorado and Utah, while various mixed sulphides are worked in Colorado. Native silver is found in conjunction with native copper in the neighbourhood of Lake Superior. According to Phillips, the annual produce of silver in the United States and territories amounts to about 1,400,000 lbs. troy, having a money value of £4,500,000 sterling.

In Central America granite, gneiss, and mica slate are the rocks most usually met with, together with an abundance of igneous rocks, which, as already pointed out in the article on Gold, are found traversing the whole western seaboard of North, Central, and South America. The mountain of Alotepec furnished 53,000 lbs. troy during the eight years from 1858 to 1865. Various other mines exist, but statistics relating to them are not accessible.

In South America valuable mines exist in Peru, Bolivia, and Chili, which might equal those of Mexico and Nevada in the amount of their yield, were it not that the excessive elevation at which they exist forms a great drawback to their value. In Peru the mines of Cerro de Pasco are most celebrated, where the ore exists in the form of *gossans;* they have been worked since the commencement of the seventeenth century, and the yield has at times been very considerable. Other districts in Peru have produced large quantities of the precious metal, the total annual produce of the Republic being estimated at nearly 300,000 lbs. troy. During the years 1784 to 1827 the principal mines of the Cerro de Pasco produced nearly 5,000,000 lbs. troy of silver, worth about £16,000,000 sterling.

The famed mines of Potosi, in the Republic of Bolivia, were discovered in 1545, and during the century following this date they yielded an annual average of 600,000 lbs. troy. Their yield has long since declined, however; and according to Whitney, there were in 1852 in the province of Potosi 1800 abandoned silver mines, and only 26 at work. Rich silver deposits are now worked in the district of Caracoles. Bolivia at presents yields about 450,000 lbs. troy.

In Chili, according to Domeyko, the veins affording gold and copper belong generally to the igneous eruptive rocks; while argentiferous copper, containing these metals in combination with sulphur, arsenic, and antimony, exist in the secondary stratified formations, prior to the upheaval of the Andes. Chloride of silver and native amalgams are usually found near the points of junction of these two classes of rocks. The richest silver district exists in the mountains north of Huasco, the most important mines being those in the neighbourhood of Copiapo. The silver ores—chiefly chloride, together with bromide and the native metal—are usually embedded in carbonate of lime and sulphate of baryta. Chili annually produces about 300,000 lbs. troy. The mines of New Granada, which were formerly of considerable value, have become unimportant.

Ores.—Silver is found native, as an amalgam or alloy, and in combination with various non-metallic elements—such as chlorine, bromine, iodine, sulphur, and selenium; it has also been detected in sea water.

Native silver occurs crystallized in cubes, octahedra, and other forms related to these; sometimes it exists in laminated, filamentous, or amorphous masses, and sometimes very minutely disseminated through the minerals. It is found to accompany all its ores, especially the sulphides and chlorides. It is met with chiefly in the primitive formations, as in granite and gneiss; more rarely in the argillaceous schists and grauwacke of the transition rocks, accompanied by quartz, carbonate and fluoride of calcium, sulphate of baryta, carbonate of iron, galena, &c.

Nearly all the localities in which silver is known to exist have produced native silver, although frequently in very small quantities. It exists in the ferruginous rocks of Brittany, and has been found at Kongsberg, in Norway, and the Saxon mines at Freiberg, as well as in Mexico, Chili, Peru, and,

associated with native copper, in the district south of Lake Superior. The native metal is always found associated with copper, iron, or gold.

In some of these localities it has been found occasionally in considerable masses. Thus at Kongsberg pieces have been extracted weighing from 50 to 600 lbs.; in America, at the end of the last century, lumps of 200 to 800 lbs. were obtained; and on one occasion a block of solid silver was discovered in the mine of Johanngeorgenstadt, which is said to have weighed 9000 or 10,000 lbs.

Vitreous Sulphide of Silver, or *Argentite*—*Argent Sulphuré*, French; *Glaserz* or *Silberglanz*, German—contains about 86 per cent. of metallic silver, and its chemical formula is therefore Ag_2S. It is of a dark lead-grey colour, may be cut with a knife, and shows a metallic lustre where cut. It crystallizes in cubes and dodecahedra, but generally occurs massive. It has a specific gravity of about 7·2, and is easily fusible, giving off vapours of sulphur, and leaving a button of metallic silver. It is met with in nature almost always combined with other sulphides, as those of copper and lead. This mineral is one of the richest and most abundant ores of silver; it forms a large proportion of that annually produced by the various continental mines, as those of Saxony, Bohemia, and Hungary, and is particularly abundant in the mines of Guanaxuato and Zacatecas in Mexico, and in conjunction with stephanite, native gold, &c., in Nevada. Its composition, according to Klaproth, is—

	From Himmelfurst.	From Joachimsthal.
Silver,	86·50	86·39
Sulphur,	13·50	13·61
	100·00	100·00

Dark Red Silver Ore, *Ruby Silver*, or *Pyrargyrite*.—*Argent Sulphuré Antimonié*, French; *Dunkles Rothgültigerz*, German.—This mineral crystallizes on the rhombohedral system, and has a conchoidal fracture. Its specific gravity is about 5·8, and according to Wöhler, it has the following composition:—

Silver,	60·02
Antimony,	21·80
Sulphur,	18·00
	99·82

A result which would indicate its formula to be Ag_3SbS_3. It is found together with calcite, native arsenic, and galena, at Andreasberg, in the Hartz; also in Saxony, Norway, Hungary, and Spain, in the Old World; and in Nevada, Idaho, Mexico, and Chili.

Brittle Sulphide of Silver, or *Stephanite*—*Argent Sulphuré fragile*, French; *Schwarzgültigerz*, German—crystallizes on the orthorhombic system, is a compound of sulphide of silver with the sulphide of antimony and arsenic, and has a nearly black iron-grey colour, a metallic lustre, and conchoidal fracture. It is generally found associated with other ores, both in Europe and in the various parts of the New World. According to the investigations of Rose and Klaproth, its composition is as follows:—

	From Freiberg. By Klaproth.	From Schemnitz. By Rose.
Silver,	66·50	68·34
Copper and arsenic,	0·50	0·64
Iron,	5·00	0·00
Antimony,	10·00	14·60
Sulphur,	12·00	16·42
Loss,	6·00	—
	100·00	100·00

From which its formula would be Ag_5SbS_4, or $5Ag_2S + Sb_2S_3$.

Polybasite—*Polybasite*, French; *Eugenglanz*, German—is another form of the brittle sulphide, which contains a small quantity of copper. It crystallizes on the same system, the crystals being short tabular prisms, and is also found massive and disseminated. It has a semi-metallic lustre and an iron-grey colour, and the scales are blood-red by transmitted light. Its specific gravity is about 6·2. It is distributed much as the last-named ore, and according to Rose the ores from Mexico and Schemnitz have the following compositions:—

	From Mexico.	From Schemnitz.
Silver,	64 29	72·43
Antimony,	5·09	0·25
Arsenic,	3·74	6·23
Copper,	9·93	3·04
Iron,	0·06	0·33
Zinc,	0·00	0·59
Sulphur,	17·04	16·83
	100·15	99·70

And its formula is $(AgCu)_9(Sb,As)S_6$.

Monochloride of Silver—*Silberhornerz*, German; horn-silver—is semi-ductile and sufficiently soft to be cut with a knife; colour, pearl-grey inclining to blue, and becoming brown in the air; has a vitreous lustre, is usually translucid, crystallizes in cubes. When pure it consists of silver, 75·3; chlorine, 24·7; and its composition is therefore represented by the formula AgCl.

This mineral, says Phillips, which was formerly supposed to be of rare occurrence, constitutes one of the richest and most abundant ores of Chili, where it is frequently associated with native silver, apparently resulting from its decomposition. It also occurs in massive amorphous fragments in connection with sulphide of silver, but still more frequently in small cubical crystals disseminated in the ferruginous rock known in Chili and Peru under the names of *pacos* and *collorados*. Specimens of this mineral, although of comparatively rare occurrence in the European mines, have been obtained from Norway, Siberia, Saxony, the Hartz, Cornwall, and Brittany.

Iodyrite, or *Iodide of Silver*, is a rare mineral of a pale lemon-yellow colour, with sometimes a tint of green. It was discovered by M. Vauquelin in the Mexican mines, and occurs in the mines of Spain and Chili, but from its rarity is of no importance as

an ore of silver. It is composed of silver 77·4, iodide 22·6.

Bromyrite, or *Bromide of Silver*, was discovered by M. BERTHIER in the Mexican minerals, where it has since been found so abundantly in the district of Plataros, near Zacatecas, that the ores there raised have received the name of *plata verde*, from the green colour which it imparts to them. It is also found in Chili and Brittany. According to BERTHIER, it is composed of silver 57·70, bromine 12·50.

Native Amalgam—Argent Amalgamé, French; *Natürlich Amalgam*, German—has a very bright silver-white colour, and is so soft as to be easily cut with a knife. It occurs both in distinct crystals, in irregular amorphous masses, and at times as thin compressed plates. It crystallizes in the regular octahedron or dodecahedron. This mineral is found in a great many different localities, but the finest specimens have been procured from Moschellandsberg in Bavaria. Its specific gravity is 14·1, and according to KLAPROTH, it contains 36 per cent. of silver and 64 of mercury, which would indicate its formula to be AgHg.

Arquerite, another species of this substance, says PHILLIPS, forms one of the principal sources of silver in the rich mines of Arqueros, in the province of Coquimbo, Chili. From its malleability and general appearance this product was for a long time thought to be metallic silver. According to the analysis of DOMEYKO, of the mining school of Coquimbo, this amalgam consists of silver 86·63, mercury 13·37; from which it appears to be composed of 12 equivalents of silver united to 1 of mercury, and its composition may therefore be represented by the formula $Ag_{12}Hg$.

Argentiferous Galena.—The sulphide of lead, or galena, is almost always associated with a small quantity of silver in the state of sulphide, and this is the source of the silver obtained in the British Islands. It is regarded as extremely rich when it contains 0·005 of silver; and in many cases the silver may be extracted with advantage when only a tenth part of that proportion is present.

In general, and whatever may be their nature, minerals are regarded as rich which contain 0·005 of metallic silver.

The other less important ores are thus enumerated by PHILLIPS:—

Hessite.—Telluride of silver.

Naumannite.—Selenide of silver.

Eucairite.—Selenide of copper and silver.

Stromeyerite.—Sulphide of copper and silver containing iron.

Dyscrasite.—Antimonial silver.

Sternbergite.—Sulphide of silver and iron.

Miargyrite.—Sulphide of silver and antimony, with a little copper and iron.

Pronsite.—Containing silver, arsenic, and sulphur.

Freieslebenite.—Antimonial sulphide of lead and silver.

Xanthoconite.—Arsenio-sulphide of silver.

Embolite.—Chloro-bromide of silver.

Selbite.—Probably a mechanical mixture of certain carbonates with other minerals which are argentiferous.

Pure Silver.—The refined silver of commerce contains a small amount of impurity, although this frequently does not exceed one-tenth per cent. The method usually recommended for obtaining pure metal consists in dissolving an alloy of silver in strong nitric acid, and adding a solution of chloride of sodium; a double decomposition occurs; the silver is thrown down in the form of an insoluble chloride, while the copper and any other metals that may be present remain in solution: 100 parts of this chloride are, when separated and dried, mixed with 70 parts of chalk and 4 or 5 of carbon, and the mixture is introduced into a crucible and raised to a white heat. Carbonic oxide is disengaged, and chloride of calcium and metallic silver remain in the crucible; or the mixture of chalk and carbon may be replaced by dried carbonate of soda.

According to Dr. MILLER, the following is the best method of preparing absolutely pure silver, such as that required in assaying as subsequently described:—"Standard silver is dissolved in nitric acid; the liquid is diluted and decanted or filtered from undissolved particles of gold or of sulphide of silver; and the solution is precipitated by the addition of chloride of sodium in slight excess. The precipitate is washed in a large jar by subsidence until the washings are tasteless. The chloride is then mixed with oil of vitriol in the proportion of 3 ozs. to each pound of chloride, and several bars of zinc are placed in the mass; the zinc is converted into chloride of zinc, which is dissolved, whilst the silver is reduced to the metallic state, and by what FARADAY showed to be a voltaic action the reduction extends through the mass. The mixture is not to be agitated. In the course of a day or two the decomposition is usually completed. If a portion of the reduced silver, after being thoroughly washed, is entirely soluble in nitric acid the reduction is complete. The bars of zinc, with the crust which adheres to them, are then carefully removed, and the reduced metal is digested for two days with dilute sulphuric acid, and is washed in a large vessel by subsidence, until the washings cease to precipitate nitrate of silver. The reduced silver is now redissolved in nitric acid and a second time precipitated as chloride, pure hydrochloric acid being employed for this purpose: the precipitated chloride is again washed by subsidence until the washings no longer redden litmus. The chloride of silver is next dried until it ceases to lose weight; 100 parts of the chloride are mixed with 70·4 of chalk and 4·2 of powdered charcoal, and the mixture is heated in a deep clay crucible. The temperature is kept at a dull red heat for half an hour, after which it is gradually raised to full redness: a considerable disengagement of gas takes place, and oxychloride of calcium is formed. The silver may be poured into an ingot mould, remelted in order to free it from slag, and afterwards rolled into sheets.

GRÄGER recommends the following method for preparing pure silver from an alloy of silver and

copper. A solution of the alloy in nitric acid is heated to 70° C., and levigated chalk is added so long as effervescence takes place, thus precipitating all the copper, while the precious metal remains in solution. It may now be treated with sodium carbonate and the precipitate ignited, after which the silver will be obtained in the metallic state on the addition of hydrochloric acid.

Chemical Properties.—At ordinary temperatures silver is not acted upon by dry or moist air; but it is tarnished if exposed to an atmosphere containing very minute portions of sulphuretted hydrogen, which is always present, to a greater or less extent, in the air of chambers heated by coal fires. When melted in open vessels it possesses the remarkable property of absorbing mechanically about twenty-two times its own bulk of oxygen, which it disengages on solidifying, producing the metallic vegetation observed on the surface of a silver button when suddenly cooled in the cupel. DUMAS has quite recently pointed out that this circumstance has not been sufficiently regarded in the determinations which have been made of the equivalent of silver as well as of those elements, such as chlorine, in the determination of which silver has been directly employed. If a mass of pure silver, after being maintained for some time exposed to the air in a state of fusion, be allowed to cool suddenly, the outer coating becomes solid, and this crust is soon broken, partly by the liberation of the oxygen which has been absorbed, and partly, perhaps, by the expansion which is said to take place when silver solidifies. This phenomenon, which is called *rochage* or *spitting*, occasions the loss of a small quantity of silver from the mass. It does not occur when the silver is alloyed with a small proportion of copper, gold, or lead; 1 per cent. of copper prevents the absorption of oxygen, to which the phenomenon is due. That this is the real cause may be demonstrated on a small scale by heating to a white red in a crucible a considerable quantity of silver, and projecting upon it a little nitrate of potassa, which by its decomposition produces an atmosphere of oxygen. The crucible is then to be covered, and the heat continued for some time, after which the lid is removed and the vessel plunged into a tub of water, placing over it an inverted bell-glass filled with the same liquid; the oxygen which is disengaged is collected in the bell-glass, and may be measured. This experiment, says BARRUEL, is not without danger, for the oxygen may be disengaged all of a sudden, and thus produce a violent explosion.

If subjected to a very high temperature, such as that produced by the oxyhydrogen blow-pipe, silver is rapidly volatilized. By inclosing some of the metal in a lime-still and directing the blow-pipe flame on it, M. STAS has succeeded in distilling a considerable quantity of pure silver. It may be interesting to note that the vapour, when condensed into fine particles escaping into an atmosphere of hydrogen, is blue by reflected light.

Silver does not absorb the oxygen of the air when it is fused with the alkalies; and for this reason silver crucibles are used in the laboratory for making analyses of silicates by means of the caustic alkalies, by which platinum would be attacked. Chlorine, bromine, and iodine combine very readily with silver, and of these three bodies iodine has the greatest affinity for it. Of the acids, nitric acts most powerfully on it, dissolving it in the cold; concentrated sulphuric acid requires heat to dissolve it. Hydrochloric acid attacks it only with difficulty, by leaving it a long time to digest; however, if the metal is in a very divided state, and the liquid be heated to ebullition, the solvent action is considerable.

Silver readily combines with sulphur, and hence the fact already stated—the facility with which it is tarnished by contact with the air containing even a very small proportion of sulphuretted hydrogen. In this case its discoloration arises from the formation of a brown film of sulphide of silver.

METALLURGY OF SILVER.—The separation of silver from its ores is effected in various ways, according to their nature. The first method consists in forming an amalgam, from which the mercury is expelled by the aid of heat; in the second, an alloy of lead and silver is formed, by methods dependent on the nature of the ore; and in the third, the metal is reduced to either a chloride or a sulphate, and deposited in the wet way.

I. AMALGAMATION.—There are four methods of amalgamation practised, the selection of the one most suited to a particular district depending mainly on the possibility of obtaining fuel. In all cases, however, the silver in the ore is first brought to the form of chloride, from which it is subsequently reduced directly by mercury, or by iron, as a preliminary step towards amalgamation proper. Much of the success of this process, however, depends on the manner in which it is conducted, and especially on certain preliminary operations which are required to bring the ore to that state of minute division in which it is most favourably circumstanced for causing the whole of the silver that is contained in it to combine with the mercury.

Mexican or Patio Process.—This method was invented by BARTHOLOMÉ MEDINA, a native of the town of Pachuca, in Mexico, in 1557; it is still practised in that country in all its primitive simplicity; and perhaps when the cheapness of labour, the poverty of the ores, the scarcity of fuel, and the deficiency even of water-power are considered, it could not be profitably superseded by any other. It will be found that its principal characteristics depend on these circumstances.

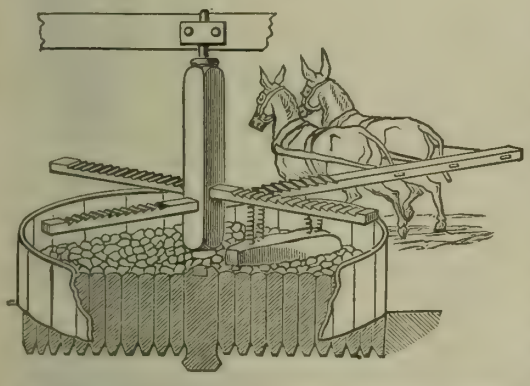
The ore, on being extracted from the mine, is placed in the hands of the *pepenadores*, men and women who break all the larger pieces with hammers; and after rejecting those in which their experience teaches them that no metallic particles are contained, and setting aside those which are very rich to be treated by the smelting process, they subject the rest to a process of crushing and pulverization, with a view to its direct treatment by amalgamation. The ores destined for this treatment are reduced to lumps about the size of the fist, submitted to the

action of the *ingenios* or stamping mills, which are either driven by mules, or, when water-power is at hand, by means of a small breast-wheel. The long horizontal shaft fixed on the axis of the wheel is armed with five or six cams, placed at different situations round the shafts, so as to act in succession on the projecting teeth of the upright wooden lifters, shod with iron, each weighing about 200 lbs., and works in a corresponding mortar, in front of which is placed a screen perforated with small round holes. It is estimated that a battery of eight of these stampers is capable of reducing to powder two or three tons of ore in twenty-four hours.

The powder thus obtained not being sufficiently fine for the purpose of amalgamation, it is transferred from the stamps to be reduced to an impalpable slime or mud in the crushing mills or *arrastres*, of the form represented in Fig. 1. These mills are commonly worked by mules, which turn a vertical shaft armed with two cross-bars. The grinding stones, as well as the sides and bottom of the mill (which should be paved with great care, no interstices being allowed to exist between the pyramidal stones), are composed of porphyry, four blocks of which revolve in each crushing mill, attached to the several arms.

The *arrastres* are usually about 12 feet in diameter, and a number are arranged in a shed; the details

Fig. 1.



of their construction will be at once understood from the engraving.

Gold is found in considerable quantities in conjunction with silver at Guanaxuato, in Mexico, and hence the grinding is conducted with more than ordinary care. From 600 to 1100 lbs. avoirdupois of the ore, as delivered from the stamps, are introduced into each arrastre, and about 110 gallons of water gradually added during twenty-four hours; at the end of which period the *lama* or argentiferous mud is baled out and removed to reservoirs, where part of the water is evaporated by the sun's heat, and the mass is then ready for treatment in the *patio*. At Zacatecas no gold is contained in the ore; each apparatus is therefore capable of grinding nearly 2000 lbs. avoirdupois in the course of twenty-four hours, since it is not necessary to reduce to such an extreme state of subdivision. A considerable quantity of mercury is lost during the process, probably in consequence of sulphide of silver being decomposed with the formation of sulphide of mercury.

The *patio* or amalgamating floor, to which the *lama* is conveyed after it has been brought to a certain consistency through the evaporation of water by the sun's heat, is represented in Fig. 2. It is

Fig. 2.



a large space, usually paved, to which a slight inclination is given in order to insure the removal of water, and in which are marked out a number of circular spaces, about 40 feet in diameter, surrounded by low stone walls or frames of wood.

At Zacatecas the *patio* is rectangular, 312 feet in length by 240 in breadth, and capable of containing 24 flat circular heaps of lama, each about 50 feet in diameter and 7 inches deep, arranged in four rows. These heaps are termed *tortas*. A small space is usually reserved at one corner for the purpose of performing assays on the ore, with the view of determining beforehand the proportion of mercury it may be necessary to incorporate with each heap.

A mass of *lama* weighing from 50 to 100 tons, according to the locality, is now introduced, and forms a layer about 1 foot thick, which is allowed to further dry until of the consistency of moderately thin mud. From 3 to 5 per cent. of salt is added, and the first treading by mules takes place, after which the mixture is allowed to rest until the following day, when mercury and *magistral* are added. This latter is prepared by roasting, in a reverberatory furnace, copper pyrites containing a considerable quantity of iron pyrites and a small quantity of common salt. The sulphates of copper and iron, mixed with some chlorides, are formed, about 20 per cent. of the whole being sulphate of copper. Usually about 1 per cent of magistral is added to each torta; but the exact amount varies according to the richness of the argentiferous ore and the season of the year. In summer, for example, and with the richer ores, about 750 lbs. to the torta, and in winter only half that quantity; for it is stated as a singular fact that in summer the mixture cools and requires more warmth, while in winter it acquires of itself additional heat. The larger proportion is for minerals containing 0·0015 of metallic silver. When the operation proceeds too

rapidly, arising from the presence of too much magistral (which would occasion a greater loss in mercury), the remedy is to add a certain quantity of lime, which serves to cool the lama.

In some localities the mass is trodden at this stage for about an hour; but it is more usual at once to distribute mercury over the surface in the proportion of about 1 lb. for every 1000 grains of silver supposed to be present. This is effected by sprinkling the metal from a bag of coarse cloth, after which the mules are caused again to traverse it at intervals for several days. The progress of the amalgamation is carefully determined from time to time by observing the aspect of the mercury obtained by washing the mineral in a bowl. During the first few days the mercury can be removed from the globule of amalgam obtained, which has a slightly grey colour, by simple pressure with the finger; and each day the amalgam obtained is more grey and more solid. If the change takes place slowly it indicates that probably an additional quantity of magistral is required; while, should the mercury become leaden, it shows that there is an excess of this substance, and the torta must be 'cooled' by adding lime. Should the amalgam obtained be extremely hard, it will be necessary to add a small additional quantity of mercury, and sometimes even a third charge of this metal is required. In summer a torta may frequently be worked off in fifteen days, while as many as forty-five days may be required in winter.

After the treading is completed, it is, at some mines, usual to add a considerable quantity of mercury to the mass in order to collect the grains of amalgam.

The next operation is the washing of the amalgamated ore, for the purpose of removing the earthy matters, and of thereby obtaining the amalgam or mixture of silver and mercury in a separate form. This is performed in *lavaderos*, or washing vats, which are circular in form, and solidly built in masonry, each about 5 feet deep and 9 in diameter.

At Guanaxuato the washing apparatus consists of three such tubs, which communicate with each other by openings at different elevations, and here no further addition of mercury is made; whereas at Zacatecas only one cistern is employed, a large quantity of mercury having been previously added. A horizontal toothed wheel, mounted on a shaft worked by mules, communicates, through the intervention of another toothed wheel, a movement of rotation to a vertical shaft placed in the middle of the vat, and armed at its lower part with four agitators consisting of cross beams, from which rise long wooden teeth to the height of 5 feet. A stream of water continually flows into the vats from a tank on a higher level. Under the action of the agitators the lighter earthy matter is kept afloat, while the heavier amalgam sinks to the bottom, and from time to time the former is allowed to flow out into a second similar apparatus, where it is subjected to a second washing, and then allowed to run away. An entire torta of amalgamated ore may thus be passed through one vat in twelve hours.

At Zacatecas a considerable quantity of amalgam results from the system of washing adopted, and it therefore becomes necessary to pass the heavier residues, collected in the vats which receive the liquid from the tub, over a washing table, after which they are roasted and returned to the *arrastre*. At Guanaxuato the agitators of the three vats are driven by the same shaft at slightly different velocities, by which the amalgam is more completely extracted. In certain districts these agitators are replaced by shovels, and the supernatant liquid is passed over riffle boxes.

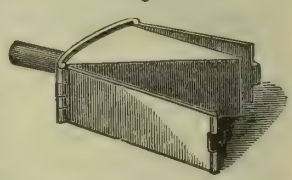
A large quantity of silver and mercury is always lost in this process, the exact proportion depending on the nature of the ores, as well as the manner of treating them. At Guanaxuato the loss is, according to PHILLIPS, from 9 to 14 per cent. of silver; at Fresnillo, often 28 per cent.; and at Zacatecas, according to DUPONT, as much as 35 to 40 per cent. The loss of mercury is about 12 or 16 ozs. for every mark (3550 grains) of silver extracted.

Fig. 3.



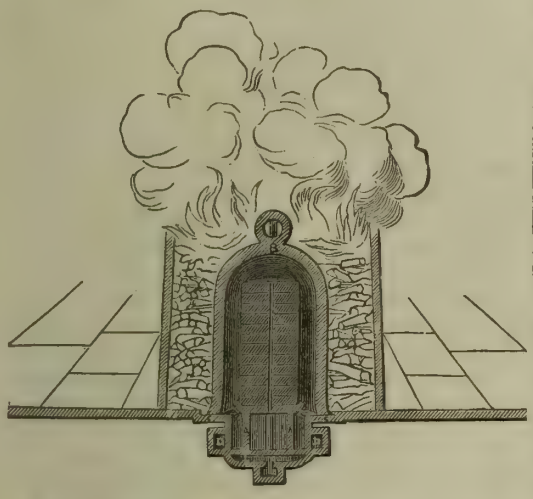
The liquid amalgam obtained in this manner, after being cleared from adhering particles of mineral, is then strained through a leathern bag (Fig. 3), the bottom of which is formed of strong canvas or thick flannel. The uncombined mercury is thus squeezed out, carrying along with it a small quantity of silver, which is not lost, as the same mercury is employed in the next amalgamating operation, while there remains in the bag a mass of semi-solid amalgam, containing about 17 per cent. of silver, which is submitted to distillation. For this purpose it is moulded into wedge-shaped masses, by means of the frame shown in Fig. 4, each about 30 lbs. in weight, and these are arranged in a circle in what is called the *burning house*, to the number of eleven, on a solid plate of cast iron having a hole in its centre. Over this row of wedges several others are built, and the whole pile is covered with a large iron bell called a *capellina*, about 18 inches in diameter and 3 feet high, lowered down upon it by means of pulleys, and carefully luted at the bottom to the iron plate with a mixture of ashes, crude salt, and lama. A loose wall of fire-bricks is then built round the capellina, leaving an interval of about a foot in width, as shown in Fig. 5, which is kept filled with burning charcoal for about twenty hours, when the bricks and ashes are removed and the capellina hoisted up. The silver is then found in a solid mass, the mercury having passed off in vapour through a pipe fixed to the opening or hole in the ground plate, by which it is conveyed into

Fig. 4.



a cistern filled with water, and there almost all condensed. The silver, which remains on the plate

Fig. 5.



in solid pieces, is weighed, and usually remelted and cast into ingots or bars, each about 80 or 90 lbs. in weight, and having an average fineness of over 99 per cent. Latterly, at some establishments cylindrical retorts of cast iron have been introduced for distilling the amalgam. The loss in mercury is usually about 1½ per cent. of the weight of silver obtained.

The rationale of the process of amalgamation, as above described, may be explained as follows:—In America the silver exists in the ores, partly in the native state, partly as a chloride, and partly as a simple or multiple sulphide. The copper pyrites which is added reacts on the chloride of sodium employed, producing sulphate of soda and bichloride of copper; the latter acts as an energetic chloridizing agent on the sulphide of silver in the ore, changing it into chloride of silver, and passing at the same time itself into the state of monochloride, which is dissolved by the solution of chloride of sodium, and in this condition reacts on the unreduced sulphide of silver, forming chloride of silver and sulphide of copper. The chloride of silver in the presence of a solution of salt is in its turn reduced by the mercury added, and by such arsenic, antimony, copper, lead, and tin as may be present, forming monochloride of mercury and an amalgam of silver. It is the monochloride of mercury so formed that is carried away by the water in the process of washing, and constitutes almost the whole of the loss in mercury. The chloride of sodium employed serves not only to transform the sulphate of copper into dichloride, but also to dissolve the chloride of silver, and thus to facilitate considerably its reduction by the mercury.

The loss of mercury occasioned by its conversion into chloride is very considerable; and it might to a great extent be avoided by employing other metals —such as zinc, tin, lead, and copper. Thus the use of an amalgam of copper has given excellent results at Guadelupe y Calvo. The copper alone is dissolved by reducing the chloride of copper in the magistral to a minimum, and the mercury thus does not act until after the complete solution of the copper. The copper employed must be about one-third of the weight of silver contained in the ore.

The following analysis of the ore in the neighbourhood of Guanaxuato is given by PHILLIPS:—

Silver,	1·04
Iron,	4·71
Copper,	0·55
Sulphur,	6·79
Carbonate of lime,	8·25
" magnesia,	3·26
Silica,	75·00
	99·60

This specimen was of more than ordinary richness, and an average sample of the ores worked by this process only contains about 0·15 per cent. of sulphide of silver, or 0·13 per cent. of the pure metal.

Stove Amalgamation.—In certain parts of Mexico the process is modified by transferring the lama from the patio (which is under a shed) when the process is about half completed, to a stove consisting of a chamber, with flues so arranged as to lead heat from a fire-place to the mixture. The heating is continued for about three days, and the mass is then returned to the shed for the completion of the patio process. The time employed is somewhat diminished, and the yield of silver increased slightly, but the loss of mercury is excessive.

Hot Process of Amalgamation.—This process, much employed in South America, but to a very small extent in Mexico, is especially applicable to ores in which the precious metal exists as a halogen salt. The ore, after being ground in the arrastre, but not to such an extreme degree of fineness as in the patio process, is transferred to a tub called a *cazo*, the sides of which slope, and are 18 inches high, and formed of wood or stone; while the base consists of a sheet of copper, about 2 inches thick and 2 feet in diameter. The whole rests above a hearth, by means of which the contents can be caused to boil. About 100 lbs. of ore are introduced, made into a paste by the addition of water, and heat is applied. From 5 to 10 per cent. of salt is now added, and the workman commences the addition of mercury, at the same time keeping the mass constantly agitated by a wooden stirrer. Mercury is gradually supplied until about twice the weight of silver the ore is assumed to contain is present, which point should be attained after the lapse of about six hours. The resulting slimes are subsequently treated by the ordinary patio amalgamation, without, however, the addition of magistral. In some districts the dimensions of the cazo are so far enlarged as to contain about 1500 lbs. The operation on this large quantity is completed in the same time as when the smaller apparatus is employed. The loss of mercury in both of these cases is far less than in the ordinary way, amounting only to 2 or 3 per cent., and this is owing to the reduction of the chloride of silver at the expense of the copper bottom instead of by the mercury.

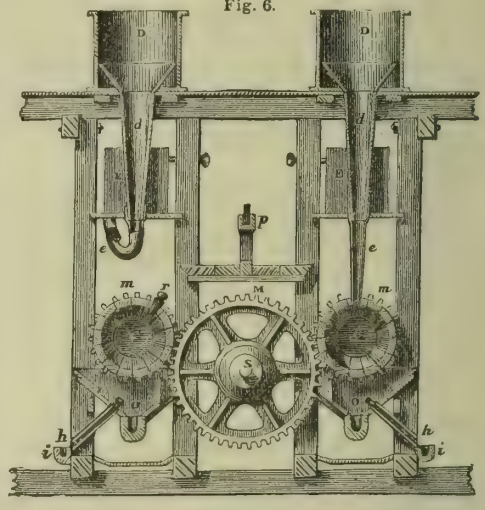
Saxon Process of Amalgamation.—It was only at the end of the last century that the method of treating silver ores by amalgamation was introduced into Europe. Here the circumstances are different to those in Mexico and Peru; fuel is cheaper, mechanical moving power is abundant; manual labour is more expensive; it is therefore important to replace the latter as far as possible by the two former, and this circumstance will explain the chief points in which the European process differs from the American. These points of difference will appear from the following account of the method of amalgamation which was practised, from 1790 to 1856, at the Halsbrücke works, near Freiberg in Saxony, the most complete establishment of the kind in Europe.

In these works no ores which contain more than 4 per cent. of lead, or 1 of copper, were submitted to amalgamation, because beyond that point the lead entering into the amalgam renders it very impure, while making the operation itself more difficult, and the copper would be entirely lost. The most usual constituents of the ores were sulphur, silver, antimony, arsenic, copper, iron, lead, zinc, &c., with several earthy minerals, and at times bismuth, gold, nickel, and cobalt. Formerly ores of different qualities were so sorted that the mixture contained an average of about 4 ozs. of silver per 100 lbs. of ore; but latterly the poor and rich ores, containing respectively about 1 and 10 per cent., were treated separately, as the amount of silver lost was then found to be less. It is necessary, also, that they contain at least 20 per cent. of sulphide of iron, to insure the liberation of as much chlorine as shall convert the whole of the silver into a chloride.

When the ore had been properly ground and mixed, a portion was laid on a large floor 40 feet in length and 12 in width, and covered with about 10 per cent. of salt; and the layers of ore and salt, when thus alternated, were thoroughly mixed by means of shovels, passed through a coarse sieve, and divided into parcels of about 4 or 5 cwts. Each parcel was then roasted in a reverberatory furnace, the floor of which was elliptical, and about 6 feet in length by 8 in breadth; the height of the vault in the centre being about 18 inches. The mixture was dried at a low heat for about twenty minutes to expel moisture, the whole being constantly stirred with a long rake, and the heat gradually raised. Dense white fumes of arsenious acid and oxide of antimony were disengaged, which deposited themselves in the condensing chambers above; after this the ignition of the iron pyrites was characterized by the appearance of a bluish flame and a strong odour of sulphurous acid. When this smell had passed away the chlorination was commenced by raising the temperature to a bright red, and maintaining it at that point for about three-quarters of an hour, or till no more gas was disengaged; and a charge was thus passed through the furnace every four hours, the mass being constantly stirred. During the first part of the operation, or the roasting properly so called, the arsenic and antimony were separated, and the sulphides of iron and copper converted into a ferric sulphate, $Fe_2(SO_4)_3$, and cuprous sulphate. These sulphates, in the second part of the process, or the chlorination, react in their turn on the chloride of sodium, producing sulphate of soda, monochlorides of iron and copper, and chlorine, which combines in the nascent state with the silver contained in the ore, thereby converting it into a chloride. Here it is the chloride of iron which principally acts as the chloridizing agent, whereas in the American process it is the chloride of copper. The roasted ore, after its removal from the furnace, was passed through a set of sieves; and the fine particles obtained, averaging about a quarter of the whole, were ground in a dry state between granite millstones. The remainder, having been mixed with 2 or 3 per cent. of chloride of sodium, was again roasted for a shorter period.

In the Saxon process amalgamation is performed in casks firmly hooped with iron, and each about 2 feet 10 inches long by 2 feet 8 inches in internal diameter. There are twenty of them, arranged in four rows, and turning on horizontal axes. Fig. 6

Fig. 6.



will give an idea of this arrangement. Attached to the end of each cask, C, C, is a toothed wheel, *m*, *m*, which engages with another toothed wheel, M, mounted on a shaft, S, driven by water-power. Each of the casks has an opening, *r*, *r*, about 4 inches in diameter, and securely closed by an iron or wooden screw stopper during the amalgamation. The roasted ore is charged into hoppers, D, D, which are prolonged downwards by conical tubes, *d*, *d*, and leather hose. *e*, *e*. The latter are introduced, during the charging of the casks, into the openings, *r*, *r*, and then turned upward as one of them is shown in the figure. Above each cask is a vessel, E, for containing the exact amount of water required for each charge, and these are fitted with flexible tubes and stopcocks for allowing the water to pass as required. The bearings of the wheels. *m*, *m*, through which motion is transmitted from the wheel, M, are mounted at the ends of the barrels, and are sup-

ported on slides which move to and fro; the wheels can therefore be disengaged at pleasure.

The charge is commenced by introducing into the barrels the water from the vessels, E, each of which contains 33 gallons; the roasted ore, to the amount of 10 cwts. for each, is then introduced, and lastly there is added from 80 to 100 lbs. of iron in pieces about 1½ inch square by three-eighths thick. The stoppers are screwed in, and the casks are thrown into gear, and made to revolve slowly for about an hour and a half at the rate of fourteen or fifteen turns in the minute. During this stage the chloride of silver dissolved in the alkaline chloride is decomposed by the fragments of iron, producing chloride of iron and metallic silver. It is very important that the roasting should have been carried far enough to decompose all the chloride of copper; for if not so, the latter would be equally reduced by the iron to the metallic state, and would subsequently pass into the amalgam, rendering it very impure. At the end of an hour and a half the barrels are stopped and water or ore added, if necessary, to bring the paste to the requisite consistency, after which 550 lbs. of mercury are introduced into each, by means of pipes connected with a tube which communicates with a large graduated iron reservoir. The barrels are then put in motion again, and this is continued for about nineteen hours without intermission, except for a short period at the end of every four hours, to examine whether the paste has the proper consistency, and to judge of the progress of the operation. The reaction is facilitated by the elevation of temperature which is observable in the contents of the barrels, and which increases with the velocity of rotation. The higher the temperature the more completely will the residues be exhausted, but the greater will be the loss in the subsequent washings of very minutely-divided mercury, which it will then be impossible to recover.

The amalgamation being now considered as terminated, the barrels are nearly filled with water, and are made to revolve during two hours with a speed of eight or nine turns per minute to collect the amalgam, when the motion is stopped, and the process of discharging proceeded with. For this purpose the conical bungs, by which they were hermetically sealed during the amalgamation, are removed, and a leathern tube fitted with an iron stopcock is inserted into each aperture; the barrels are reversed, so that the apertures are turned downward, and the amalgam is made to fall along the sluice, *h*, into the gutter, *i*, which conducts it to a general reservoir. The barrels are then turned up, to adjust to them hollow stoppers fitted with wire-grating; and on reversing them again the slimy residues fall into the canal, O, to be conducted to the washing vats, while the pieces of iron are retained in the barrels by the grating. Altogether each operation lasts twenty-four hours, and about 2 lbs. of iron are consumed in each barrel.

The earthy residuum of the barrels in which the amalgamation was performed is run into five circular tanks, each about 5 feet in depth, the diameter of which is 5 feet at the top and 3 at the bottom, and these are filled up with water; in the side of each are four orifices, arranged one over the other about 5 inches apart. In the middle of each tank a vertical axis, carrying horizontal arms, is made to revolve during twenty hours at the rate of twelve to fourteen turns per minute; and while this agitating process is going on, the supernatant liquid, containing the lighter earthy impurities, is allowed to flow out, twice by the highest orifice, twice by the second, and once by the third or lowest, taking care to fill up the tanks with water after each partial discharge. The amalgam itself is drawn out by the lowest orifice once a week, and after being fused yields an alloy containing from 25 to 65 per cent. of fine silver. If the solid matter which settles from the water drawn off contain on assay 4½ ozs. per ton, it is dried and roasted again with 15 per cent. of pyrites and 5 of salt, and treated in the manner already described.

The total loss in silver varies from 5 to 9 per cent. of the quantity contained in the ore; the loss in mercury amounts to 25 per cent. of the silver obtained, and, from an average of twenty years, is thus distributed:—

Loss in mercury, which remains in the earthy residues of the amalgamation,	21·78
Loss in the distillation of the amalgam...	2·77
Loss proceeding from the cracking or breaking of the bells,.....	0·45
	25·00

Distilling the Amalgam.—The mercury is then separated from the silver by distillation; and for this purpose iron bells, analogous to those employed in Mexico, were formerly used. Latterly, however, these were almost entirely superseded at Freiberg by iron retorts, in which 450 lbs. of amalgam was placed on iron plates. The retort was provided with a large condensing tube, in order that the mercury might be collected without the aid of water. Each charge required about ten hours for its complete distillation, and yielded about 70 lbs. of *teller-silber*, which, after having been melted in an iron crucible and cast into an ingot, contained about 80 per cent. of the precious metal.

The process was ultimately abandoned at Freiberg on account of the expense which it entailed and the unsatisfactory nature of the results obtained, and the argentiferous ores are now smelted with others containing lead, in the manner presently to be described; it was, however, in use at Huelgoet in Brittany as recently as 1865.

Modification of the Barrel Process of Amalgamation employed in Spain.—A modification of the method above described, in use at Constante in Spain, must be briefly noticed. In the ores there treated, which come from the mines of Hiendeloencina, the silver exists principally as an antimonial sulphide, disseminated through a gangue containing a large quantity of sulphate of baryta. The ore having been thoroughly crushed is mixed with 5 or 6 per cent. of salt, and gradually introduced, by a hopper in the centre, into a circular calcining furnace, the

floor of which rotates at a rate of three or four revolutions per hour, the ore being caused to pass from the centre towards the edge by fixed iron rakes. About 8000 lbs. of ore are treated in each furnace in the course of twenty-four hours.

It is important to observe that ores can only be treated in this manner when they contain iron pyrites, as this, after being partially converted into sulphate, reacts on the salt and liberates chlorine. The calcined ore is now passed through a series of sieves of sixty holes to the linear inch. The lumps finally obtained are returned to the furnace, and the fine ore introduced into the amalgamation barrels. About 1300 lbs. are introduced into each, together with 320 lbs. of water and 100 to 150 lbs. of iron. After the barrels have revolved slowly for two and a half hours they are stopped, and, if the mass be of the proper consistency, 400 lbs. of mercury are introduced into each. They then rotate at about double the initial rate for sixteen hours, are again stopped and filled with water, and after two more hours' rotation are emptied in a manner very similar to that already described, except that the barrels continue to rotate. The amalgam, having been strained in canvas bags, is retorted, and the silver so obtained is melted, refined, and cast into ingots.

Washoe Process.—It became evident soon after the discovery of the Comstock lode that the methods practised in other localities for treating the ores of silver could only be practised with profit on the richer class of ores there produced, and, moreover, the climate of Nevada exercised a prejudicial influence on the chemical action of the torta. It was therefore necessary to devise a method more adapted to the special circumstances under which the ore was obtained. The method finally adopted consists in the employment of stamps, pans, &c., similar to those already described in the article on GOLD. It will be unnecessary, therefore, to give a detailed account of such apparatus as has been there referred to.

The veinstone of the Comstock consists principally of a crumbling white quartz, and this generally contains clay, iron and copper, pyrites, and small quantities of blende, galena, and argentite; occasionally, also, polybasite and stephanite.

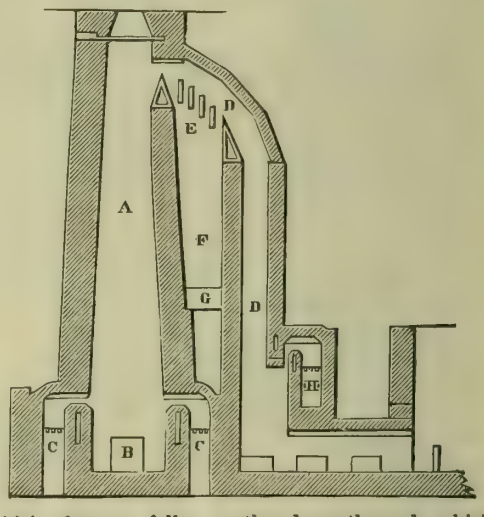
The ore is first broken into fragments about the size of a walnut, by means of sledge hammers or BLAKE'S rock-breaker. It then passes direct to the mill, where it is crushed, with the addition of a considerable quantity of water. On the side of the mortar opposite to that at which the ore is introduced is fixed a screen of Russian sheet iron, perforated with holes from $\frac{1}{24}$th to $\frac{1}{40}$th of an inch in diameter. Each stamp is usually capable of crushing 2 tons of ore of average quality in twenty-four hours.

On leaving the mill, the pulp passes along troughs to "settling" tanks, a number of which are arranged in front of the screens. They are constructed of planks, and are 6 or 7 feet square and 3 or 4 feet deep, and arranged in series in such a manner that when one is nearly full, the stream passes through an aperture to the next, and the stream which finally escapes is tolerably clear water. This still contains crushed ore, and is therefore conducted to a large pond or to a second series of settling tanks.

The "slimes" collected in the first series are now transferred to the pans, which vary much in their details of construction, any of those referred to in the article on GOLD being employed.

In mills of more modern construction, what is known as a Stetefeldt furnace is employed, and into this the ore passes, after being ground in the stamps, in order that all the silver present may be converted into chloride. The introduction of the Stetefeldt furnace represents a very great advance in the metallurgical treatment of silver. It is based on the fact, first observed by STETEFELDT, that silver ores in a state of moderately fine powder (no matter in what combination the silver occurs), if mixed with salt, are completely chloridized on falling against a current of hot air which rises in a properly arranged shaft. The general appearance of the furnace will be at once understood from the accompanying Fig. 7, in which A represents the shaft through

Fig. 7.



which the ore falls; B, the door through which roasted ore is discharged upon a cooling floor; C C, the fire-places; D, the flue for the gases to pass out of the shaft, A; E, a grate of cast-iron plates, forming the base of the flue, D, and allowing much of the dust that escapes from A to fall into the chamber, F; G, discharge door; H, furnace for roasting dust in the flue, D.

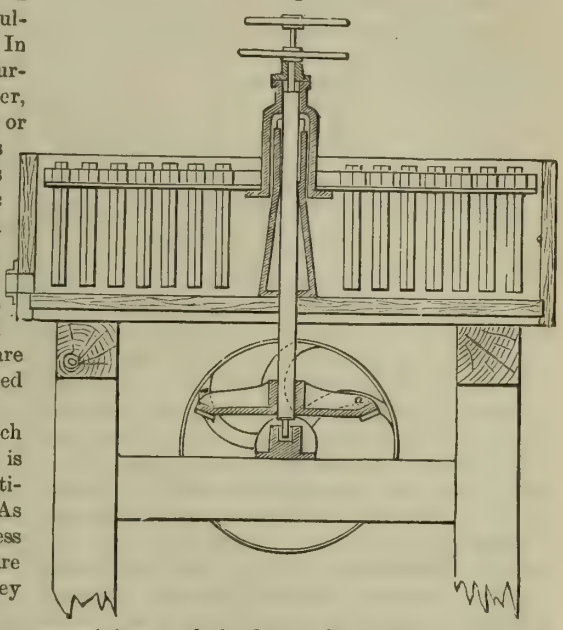
The ore having been mixed with from 3 to 6 per cent. of salt (according to its richness) on a kiln, is crushed in a dry battery; and after any lumps accidentally present have been removed by a revolving screen, the mass is transferred by an elevator to the top of the furnace. It is then introduced by a specially-devised hopper into A. The fire is kept as nearly as possible the same in all the furnaces, the heat being such that the roasted ore is just red-hot; and when nearly a ton has accumulated, the

mass is removed through the door, B. KÜSTEL explains the chemical action in this furnace as follows:—As soon as the ore enters the furnace, each particle ignites, evolving sulphur, which, in presence of atmospheric air, is converted into sulphurous acid, and the metal into an oxide. In contact with ore particles and oxygen, the sulphurous acid becomes sulphuric acid, which, however, does not combine with the metallic oxide, or only to a very slight degree, but immediately acts on the salt, and liberates chlorine. As steam is present from the burning of the fuel, hydrochloric acid is at once formed, and the furnace is thus filled with chlorine, hydrochloric acid, sulphuric acid, sulphurous acid, oxygen, steam, and volatile chlorides of base metals. These are all in the gaseous condition, and combine to act on the sulphurets and oxides with great energy. Thus, if the particles are sufficiently minute, they cannot fail to be chloridized before reaching the bottom of the shaft.

The furnace is capable of treating ore which contains nothing but silver-bearing galena, and is specially applicable when large quantities of antimonial and lead-bearing minerals are present. As a general rule, the richer ores are more or less associated with galena, &c., and they thus require a preliminary roasting in such a furnace before they can be submitted to the process of amalgamation.

The method followed varies considerably in different mills, but the following was the method adopted at the Eberhardt and Aurora mines, in White Pine County, in 1872:—About 2300 lbs. of pulp, with water enough added to keep it in a tolerably thick condition, is charged into each pan (of the Wheeler and Varney construction); 1 per cent. of salt, or about 25 lbs., is then added, with 2 ozs. of sulphuric acid, and from one-half to 1 lb. weight of sulphate of copper. The temperature of the pulp is maintained at about 160° Fahr. by introducing steam below the false bottom of the pan. The mullers having been lowered, the pan is caused to grind the pulp at a rate of rotation of about 60 revolutions per minute for three hours, at the end of which period from 150 to 200 lbs. of mercury are added, and the grinding is continued for an additional three hours. The mullers are then raised, and about 2 lbs. of carbonate of soda added, in order to "clean" the mercury, and two hours' further grinding completes the pan process. The contents are then run off into the "settlers" (already described, under GOLD), and allowed to remain for three-quarters of an hour. The settler is then filled with water, allowed to cool down, and when at the proper temperature, plugs are withdrawn, and the liquid run off to the "agitators," a stream of cold water being introduced all the time. The agitator resembles both the pan and settler, but is of somewhat larger dimensions, and is driven in a different manner. A section of this apparatus is shown in Fig. 8. It consists of a round tub formed of wood, in the centre of which rises a hollow cast-iron cone,

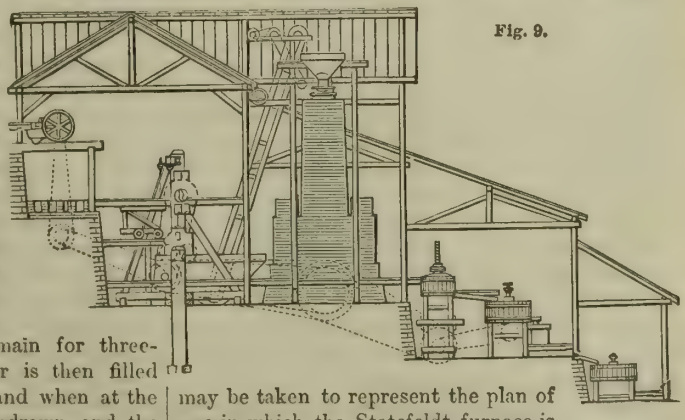
Fig. 8.



containing a shaft driven by gearing below. A cast-iron cap rests on the top of this shaft, from which project iron arms carrying wooden stirrers hanging vertically, and reaching nearly to the bottom of the tub. A copious stream of water is introduced all the time the machine is in action; and the pulp being thoroughly beaten up and thinned, the lighter parts flow off with the current, while the amalgam and "floured" mercury fall to the bottom. This amalgam is always poorer and less pure than that which collects in the settler.

The mills are of course arranged in very various manners in the different districts, but Fig. 9

Fig. 9.



may be taken to represent the plan of one in which the Stetefeldt furnace is employed. It will be sufficient to indicate the several appliances in such an establishment, where the ores are crushed in a dry state. After passing through a BLAKE'S rock-breaker, the ore is conducted to the stamping floor or self-feeder, to be supplied to the

stamps, a drying floor being interposed when necessary. On leaving the stamps, the powder is carried by a bucket-lift, which raises it to the pulp-feeder at the summit of the furnace. From this it is drawn on to cooling floors, and goes to the pans, thence to the settlers and agitators, and is finally collected outside the mill in the settling vats.

In the White Pine district about 60 per cent. of the ore contains silver in the form of chloride, the remainder being principally sulphide; the gangue is quartz containing a large quantity of carbonate of lime.

The "chemicals" introduced into the pan vary considerably in different establishments. The following is supposed to be the reaction which takes place when the operation is conducted as above described:—Binoxide of manganese being present in the ore, the reaction which takes place between it, the sulphuric acid, and the common salt, liberates chlorine, which converts the lower metals into chlorides. The action of the acid on the iron shoes of the pan also produces sulphate of iron, and this, with the sulphate of copper added, forms magistral, which acts in the same manner as in the Patio process, producing chlorides of copper and iron, which assist in reducing the silver to the form of chloride. The chloride is then reduced to the metallic state, by the action of the iron of the pan itself, and amalgamates with the mercury. The addition of carbonate of soda is of very doubtful advantage. The sodium amalgam already described (see Article Gold, vol. ii.) is probably the best means of insuring the amalgamation, but in its absence cyanide of potassium is an excellent substitute. Many practical men consider that, with a pan which insures a thorough circulation of the pulp and good working, the "chemicals" may be advantageously dispensed with; and it is asserted that galvanic currents, occurring within the pan, have much to do with the decomposition of the silver compounds. The following is the theory of the action in the pan given by J. D. Hague in his valuable work on the "Mining Industry of the Fortieth Parallel:"—

The ores treated consist chiefly of native gold, native silver, and sulphides of silver, associated with varying proportions of blende and galena. The chloride of sodium and sulphate of copper react and form dichloride of copper. The metallic iron present partially reduces this to the state of monochloride.

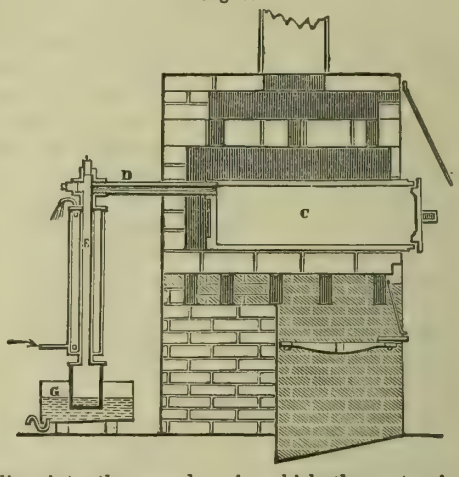
Both chlorides of copper assist in reducing the ores.

Sulphate of copper augments the amalgamating energy of mercury by forming small quantities of copper amalgam, and it tends to remove lead from the mercury.

Mercury and iron, under the influence of heat and friction, are, however, the principal agents in the reactions which take place.

The amalgam, having been strained in bags in the manner already described, is placed in lumps in cast-iron semi-cylindrical trays, which are introduced into horizontal iron retorts arranged as represented in the annexed Fig. 10. The retort itself, C, is 12 inches in diameter and 3 feet long, and is provided with a close-fitting stopper, like that of a coal-gas retort. The interior is connected by the pipe D with a Liebig's condenser, E, the condensed mercury

Fig. 10.



falling into the vessel G, in which the water is at such a height as to admit air into C before a column of water can ascend to the level of the tube D. The tubes are so arranged that by removing stoppers at the angle, they can be cleaned with ease. The interior of the retort is coated with a thin wash of clay or milk of lime, to prevent adhesion of the amalgam to the iron. About 1000 lbs. of amalgam are introduced at once, and the temperature gradually raised; the crude bullion, generally weighing about one-sixth of the original amalgam, is broken up, melted, and cast into ingots.

II. Smelting and Cupellation. — The second great subdivision of the methods adopted for extracting silver from its ores comprises, as already mentioned, all those processes by which the precious metal is first brought into the form of an alloy with lead (a metal which has as great an affinity for silver when in a liquid state as mercury itself has), and subsequently extracted by cupellation, which may or may not be preceded by concentration.

Smelting.—It will be impossible in the limits of this article to give even a complete summary of the numerous methods adopted for the smelting of silver ores containing lead, with or without copper, as the system practised is in no two places precisely similar, depending, as it does, so much on the special resources of the district. Many of the methods are extremely complicated, and they are now generally disused, having been replaced by one or another of the methods of Class III. We cannot do better than refer the reader who desires complete information to Phillips' "Mining and Metallurgy of Gold and Silver," from which a considerable portion of the information which follows has been derived.

In Lower Hungary the poorer silver ores, containing a considerable quantity of pyrites, were formerly treated successively in three furnaces provided with tuyeres, through which a current of air is driven on to the hearth containing the ore mixed with a flux. The slags pass over the breast of the

hearth, and the remaining matt is left in an enriched condition. In the third furnace operation a quantity of lead, depending on the richness of the ore, is introduced, and this takes up a large quantity of the silver and gold contained in the ore—usually from 400 to 600 ozs. per ton. The slags from this fusion, containing about 150 ozs. per ton, are again passed through the furnaces.

The precious metals are subsequently extracted from the lead in one of the cupellation furnaces already described (see Article LEAD, vol. ii., page 298).

At Freiberg, previous to the introduction of AUGUSTIN'S process, a method analogous to this was practised; the principal difference consisting in the use of roasted lead ores in place of the bath of melted lead. As it has been discontinued, however, it will be unnecessary to do more than refer to it.

At Clausthal, in the Hartz district, the lead ores being rich in silver, it is difficult to enrich them by simple mechanical treatment; and they are therefore fused in a blast furnace, after being mixed with a certain proportion of granulated cast iron. The lead is reduced to the metallic state, and the liberated sulphur combines with the iron; the molten lead thus takes up a considerable portion of the silver present. It is run off, and subsequently desilverized, the precious metal remaining in the matts being extracted by four successive fusions.

The Castilian furnace (see article LEAD, vol. ii. page 288) is very generally used for treating low-produce argentiferous galenas. In this the lead ore is partially roasted prior to its fusion with iron, instead of being introduced direct into the furnace in the manner formerly practised at Clausthal.

The argentiferous galena, containing a considerable quantity of silica, obtained at the mines of Pontgibaud, in the department of Puy-de-Dôme, in France, is treated in a manner peculiar to that district. PHILLIPS points out that the gangues are analogous to those met with in Mexico, Nevada, &c., and that the method, as described below, is peculiarly applicable to the treatment of such ores where fuel and ores of lead are to be obtained at a moderate cost.

The ore is delivered at the smelting works thoroughly crushed, so that it will all pass through a sieve of about six holes to the linear inch. It is passed through no less than nine distinct operations, and, in addition, four operations are necessary for the treatment of the residues obtained.

The principal processes are:—1, Preparation of *lits de grillage;* 2, roasting; 3, preparation of *lits de fusion;* 4, smelting in Castilian blast furnace; 5, improving; 6, crystallizing; 7, refining; 8, reducing; 9, resmelting rich slags; and there are several subsidiary processes. It will not be possible in the limits of this article to give more than a brief account of each of the above operations.

1. Uniformity of composition of the ore is very important for the successful carrying out of the process; and as it would be impossible to manipulate the large masses treated so as to form a uniform admixture, the device known as a *lit de grillage* is resorted to. The *lit* is formed by spreading weighed portions from the several parcels of ore in thin layers, one over the other, until a total weight of about 20 tons (the amount roasted per day) has been taken, and the portions so taken are such as to exhaust all the parcels at the same time. The charge is then obtained by cutting in a vertical direction through these several layers. Matts resulting from previous washing operations in the blast furnace are also introduced into the *lits.*

2. The *roasting* is conducted in reverberatory furnaces of great length and width, capable of working a total charge of 6 tons at a time. The ore is introduced through hoppers at the part of the furnace most distant from the fire-place; and after it has been dried, it is advanced by means of paddles to the central, that is, the desulphurizing or oxidizing portion, whence it passes to the agglomerating bed on a somewhat lower level. On reaching this latter the ore is fused, and a charge is withdrawn at the end of every six hours, when a fresh charge of 2 tons is introduced through the hoppers.

3. The *lits de fusion* are prepared in a similar manner to the *lits de grillage*, but consist of roasted ore, scrap iron, limestone, and fluor spar.

4. The Castilian furnace has already been sufficiently described in the article LEAD, and it is not necessary to specially refer to the form used at Pontgibaud. Suffice it to say, that the ore is arranged round the sides, while the coke is at the centre and against the breast. Care is taken to prevent the flame rising above the surface of the charge. From 5 to 6 tons of lead can be obtained from such a furnace in a day of twenty-four hours, together with from 7 to 10 per cent. of matt.

5. The lead thus obtained must be prepared for crystallization by the Pattinson process by being placed in a specially constructed reverberatory or "improving" furnace, where it is partially oxidised at a low red heat. By this means such impurities as antimony, sulphur, arsenic, &c., are removed, and the lead is rendered 'soft.' After a charge of 20 tons has remained in the furnace for sixty hours, the metal is run off by opening a hole in the bottom of the pan, while the dross, which contains a considerable quantity of silver, is treated in the reducing furnace.

6. The method of crystallizing by the Pattinson process has been already described in considerable detail in the article LEAD: it need only, therefore, be added that at Pontgibaud the method of *thirds* is practised, and that it is found to be impossible to enrich the lead beyond 2 per cent. of silver.

7. The *refining* takes place in a furnace which differs but little from the ordinary English cupellation furnace. At the end of the operation the silver is cast into moulds and remelted in black-lead crucibles, when it yields metal assaying 999-thousandths.

8. The *reduction* of the litharge, pot dross, &c., takes place in a kind of reverberatory furnace, and the amount of lead thus reduced is very great.

9. Finally, the slags are smelted in a blast furnace similar to that used for the ore.

Smelting is resorted to in some parts of Mexico in place of the Pattinson process; but only in the case of the richer class of silver ores.

They are first roasted in heaps or in circular kilns, the charge for the latter consisting of about 2000 lbs. of ore, roughly broken and mixed with one half of its weight of dry wood, and the subsequent fusion with fluxes and litharge takes place in a small blast furnace, charcoal being usually employed as a fuel. When a sufficient quantity of argentiferous lead has accumulated, it is withdrawn by raising a dam between the breast and a receiving basin, and the matts collect on the surface.

Cupellation.—The treatment of argentiferous lead ores, with a view to the separation of the silver, has been fully described in the article Lead.

Very poor leads cannot be directly cupelled with profit, because the value of the silver obtained does not defray the expense of the operation. In that case recourse is had to Pattinson's process for the extraction of silver, which has also been fully described in the article Lead (vol. ii., page 292); and after the lead has been enriched by successive crystallizations, it is fit to be cupelled.

Liquation.—The matts obtained in treating cupriferous minerals were formerly, at Mansfeld in Saxony and in the Hartz, subjected to a treatment termed *liquation*, with a view to extract the silver contained in them. This has, however, been generally replaced by one of the methods of chlorination or sulphurization, soon to be described. It is based on the circumstance that when argentiferous copper together with lead is heated to about 500° C., the lead runs off and carries with it the greater part of the silver present.

Amalgamation of Copper Matts. — At Mansfeld also formerly, and at Cziklova in the Banat, a system of amalgamation was practised. In the latter locality the process comprises four distinct operations. The coarse copper having been reduced to a fine powder is mixed with iron pyrites and salt, roasted, and again pulverized. After being moistened with water the mixture is introduced into barrels, together with lumps of black copper, and treated with mercury in a manner very similar to that already described.

Wet Methods for the Extraction of Silver.—There are four principal processes for extracting silver from ores in which it exists, either in the native or combined state, by forming a soluble compound, and subsequently removing the metal by precipitation. In the methods devised by Augustin and Von Patera the silver is converted into a chloride, while in those of Ziervogel and Karsten the sulphate is obtained.

Augustin's Process.—This is founded on the fact, well known to assayers, that chloride of silver is soluble in a solution of common salt, especially if the latter be in a concentrated and heated condition. It was employed at Freiberg for treating argentiferous copper matts from 1849 to 1862, when a sulphuric acid method was adopted. It is necessary that lead, zinc, antimony, and arsenic be not present, except in very moderate proportions, in the ores treated by the method of Augustin.

The matt having been finely ground and sifted, is roasted for five hours at a low red heat in a reverberatory furnace, when it is transferred to a second hearth and roasted for a similar period, so that most of the silver is converted into a sulphate. The charge having been withdrawn, is ground, and after mixing it with about 4 per cent. of salt, the whole is returned to the same furnace. The roasting converts the silver into a chloride, as in many of the processes already referred to; and after two or three hours the mass is transferred to the premises in which the lixiviation takes place.

A series of wooden tubs, provided with false bottoms covered with twigs, are each filled with about 8 cwts. of the roasted matt and supplied with hot brine, which dissolves the chloride on passing through the mass, carrying it through the filters to a trough by which it is conducted to a large reservoir. Thence it is led to a set of tubs containing metallic copper; this causes the silver to be precipitated in the metallic state, and it is subsequently washed with hydrochloric acid and water, pressed into balls, dried, and passed on to the refinery.

Von Patera's Process.—This is founded on the fact, first pointed out by Percy, that the chloride of silver is soluble in hyposulphite of one of the alkaline metals, from which it may be deposited by any alkaline sulphide, hyposulphite being reproduced. The process was first introduced in 1858 in the works at Joachimsthal, where it is still practised.

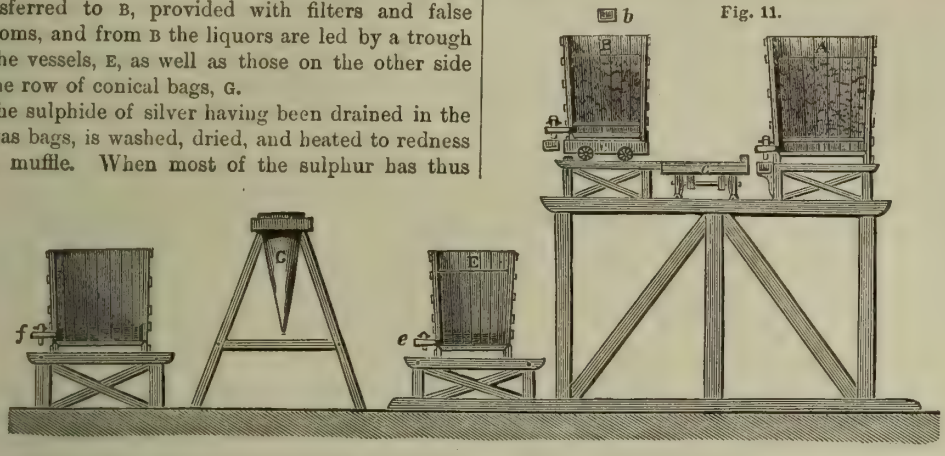
It comprises four distinct operations. The ore having been coarsely ground, is roasted in a furnace with a wide hearth, the heat being raised gradually; steam is introduced on the mass attaining a red heat, and the whole withdrawn at the end of four hours. After being thoroughly ground and mixed with about 9 per cent. of salt and 2 or 3 of sulphate of iron, it is placed in a similar furnace, and steam is introduced in the same manner as before; in about twelve hours it is removed to the lixiviating department. After being treated for six hours in one set of tubs with hot water, in order to remove soluble chlorides and sulphates, such as those of copper, zinc, iron, nickel, and cobalt, the mass is transferred to a second set, where it is washed with a cold solution of hyposulphite of soda, of such a strength that each cubic foot is capable of holding in solution 0·753 lbs. of silver; this solution then passes from below the false bottoms of the tubs to the precipitating vats.

A solution containing polysulphide of soda, with a small amount of hyposulphite, and prepared by fusing soda-ash with sulphur and subsequently boiling the product, is now introduced so long as a precipitate is formed; care must be taken, by successive trials, that neither the argentiferous nor the precipitating solution remains in excess, as the resulting supernatant liquid would then be less fitted for use as a solvent when again employed. The system of vats employed in the lixiviating

department is shown in Fig. 11. A represents one of a series of tubs into which the roasted ore is introduced with water. The insoluble mass is transferred to B, provided with filters and false bottoms, and from B the liquors are led by a trough to the vessels, E, as well as those on the other side of the row of conical bags, G.

The sulphide of silver having been drained in the canvas bags, is washed, dried, and heated to redness in a muffle. When most of the sulphur has thus been removed, the mass is fused in large crucibles, with the addition of metallic iron to remove the

Fig. 11.

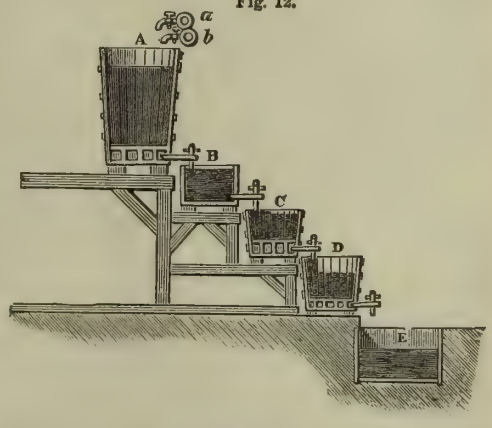


remaining sulphur. The metal obtained, containing about 95 per cent. of silver, is then sent to be refined.

Ziervogel's Process.—Since 1857 the method devised by Augustin has been replaced by the cheaper and simpler process now about to be described. It is based on the fact that sulphate of silver is soluble in water, and that it requires a higher temperature for decomposition than any of the other soluble sulphates of heavy metals, which are produced during the roasting, with pyrites, of copper matts containing silver. It is, however, not generally applicable to the treatment of ores containing zinc, lead, antimony, or arsenic. The matt having been reduced to a fine state of division by millstones, is roasted, together with about 12·5 per cent. of imperfectly desilverized residues and 4·5 per cent. of lixiviated lumps, in a specially constructed furnace with two hearths, one above the other. The upper one, into which the mass is first introduced, is closed, and forms a kind of muffle, while the lower one is in free communication with the fire-place and chimney. After the mixture has remained undisturbed for half an hour on the upper hearth, nearly 1 per cent. of dry powdered lignite is added, and the whole stirred with a rake. After thorough stirring and uniform heating for about five hours, an additional 4·5 per cent. of powdered lignite is added, and the whole, while glowing, is transferred to the lower hearth. Here the roasting is continued for about two hours, its progress being ascertained by withdrawing a small quantity of the mass, and testing with water, until no greenish coloration is obtained. The heat is now raised by using a fuel which does not give a smoky flame; and the mass is ascertained to be sufficiently roasted when the liquid obtained by lixiviating a small quantity has a light blue colour, yielding a dense precipitate of silver on addition of salt. This stage of the roasting usually occupies rather over five hours.

The mixture is next transferred to tubs similar to those previously described, and treated with hot water, slightly acidulated with sulphuric acid. The liquor which escapes is conducted to another series of vats, where it is precipitated by means of cement-copper; and the resulting finely-divided silver is lixiviated with dilute sulphuric acid, in order to remove gypsum and salts of copper. The series of vats used in this case is shown in Fig. 12. A repre-

Fig. 12.



sents the row of vessels that receive the powdered mixture; B, a long trough into which the silver solution passes; and C, vats containing cement-copper. D also contains copper for precipitating the last traces of silver, and the spent liquor is received in a lead-lined cistern, E. The washed metal is dried and refined.

The following interesting table is given by Dr. Lamborn in his "Metallurgy of Silver and Lead:"—

Extraction of Silver by	Cost. £ s. d.	Amount of Silver Left in Copper. Per Cent.
Liquation, from 1 cwt. of copper,	1 10 0	0·100
Amalgamation, "	16 6	0·059
Augustin's process, "	13 6	0·059
Ziervogel's " "	7 6	0·029

Karsten's Process.—This method is practised at

Oker, in the Lower Hartz, for removing silver and gold from copper matts or granulated copper, and consists in removing the copper as sulphate by means of sulphuric acid, diluted with its weight of water, and heated to about 70° C., and subsequently smelting the metallic mud obtained with litharge. The argentiferous lead, containing about 2 per cent. of silver, is subsequently cupelled.

Claudet's Process.—This was devised for extracting silver from the lyes obtained by treating copper pyrites, after roasting and chlorination, with water, which usually contains about 1 part of silver to 10,000 parts of water. The solution having been mixed with iodide of potassium, or some other soluble iodide, is diluted, when iodide of silver is deposited, together with some salts of copper and lead. The silver is then reduced by means of metallic zinc, the resulting zinc iodide being used as a precipitant subsequently.

Combinations of Silver.—There are three oxides of silver—a suboxide, a monoxide, and a dioxide. Of these the monoxide alone forms permanent and definite saline combinations.

Argentous Oxide, Ag_4O, was discovered by Wöhler in 1839. It may be obtained by heating citrate of silver to 100° C. in a current of hydrogen, taking up the resulting compound with water, in which it is sparingly soluble, and adding hydrate of potash. It is a black, unstable solid, which does not assume a metallic lustre under the burnisher.

Monoxide of Silver, *Argentic Oxide*, Ag_2O, may be obtained in various ways. The most usual consists in mixing concentrated hot solutions of potash and nitrate of silver, when the oxide is at once obtained as a black powder, which may be washed. The precipitate has a density of 7·143, according to Herapath; when washed, it is of a brownish-grey colour, anhydrous, and soluble in about 3000 times its weight of pure water; and it has, when in solution, an alkaline reaction, and a nauseous metallic taste. It is completely reduced to the metallic state by being raised to a red heat, or even by the prolonged action of solar light. In the latter case, however, the black powder which results is possibly the suboxide.

It is a very powerful base, and, according to Rose, capable of absorbing the carbonic acid from the air when in a moist state; in combination with the fusible silicates it is sometimes employed for producing yellow glass. According to Böttger, sulphide of gold, moist flowers of sulphur, selenium, amorphous phosphorus, and other substances, are ignited when rubbed in contact with it. By digesting it with caustic ammonia, or by dissolving nitrate of silver in ammonia, and subsequently adding potash, an extremely detonating compound, known as *fulminating silver*, is formed; which is very dangerous, often exploding, even when moist, if subjected to the slightest friction, and its composition has not therefore been ascertained. Some consider it to be an amide or nitride of silver, while, according to others, it is a combination of argentic oxide with ammonia. This compound, which must not be confounded with the *fulminate of silver*—to be described presently—has hitherto received no application, on account of the danger which attends its preparation and management.

Silver Dioxide, *Peroxide of Silver*, Ag_2O_2, was obtained by Ritter by the electrolysis of a weak solution of nitrate of silver. It deposits in acicular crystals at the positive pole, and has a density of 5·474; it is readily converted into the protoxide, and is of no use in the arts.

Chlorides of Silver.—There are two chlorides of silver, the argentous and argentic chloride; the latter of these, however, is the only one of importance.

Argentous Chloride, *Subchloride of Silver*, Ag_2Cl, is formed by treating argentous oxide with hydrochloric acid, or by precipitating citrate of silver with common salt, and it is formed by the action of light on the higher chloride. It is a brown powder which turns black on drying.

Argentic Chloride, *Chloride of Silver*, AgCl, occurs native as horn silver, and is produced by adding a solution of chlorine, of hydrochloric acid, or of any soluble chloride, to nitrate of silver, or to any of the solublesalts of silver, with the exception of the hyposulphite. Thus—

$$AgNO_3 + HCl = AgCl + HNO_3.$$

It falls in the form of a curdy white precipitate, which by exposure to light becomes purplish-brown, and ultimately black. In sunshine the change is extremely rapid, more especially if any organic matter be present. The presence of moisture is necessary to the blackening effect of light upon the chloride, as when dried in the dark and subsequently exposed to light under an inverted glass over sulphuric acid, no discoloration is produced.

This change is probably due to partial liberation of the chlorine, argentous chloride being formed; and it is the foundation of the extensive use which is made of the silver salts in photography. It is almost perfectly insoluble in water, so that the minutest portion of hydrochloric acid, or of a chloride in solution, may be detected by adding to the liquid a drop or two of nitrate of silver. The converse reaction is taken advantage of for assaying silver in the humid way, in the manner subsequently described. It is soluble in hot hydrochloric acid, and in strong solutions of the chlorides of the alkalies and the alkaline earths. This fact is applied to the extraction of silver from its ores in the Augustin process; and its solubility in the hyposulphite of the alkalies is applied in Von Patera's process; both of these have been described.

It is easily soluble in ammonia, and on evaporating the solution the chloride is obtained in the form of octahedra. When dry chloride of silver is heated to dull redness in a silver crucible, it fuses, and on cooling concretes into a grey semi-transparent substance, which is known as horn silver, or *luna cornea*.

Iron, zinc, and such other metals as are easily oxidised, reduce the moist chloride to the metallic state. These metals are, therefore, generally employed for obtaining pure silver, as already explained at page 739. Iron, however, is perhaps preferable

to zinc, on account of the great difficulty experienced in removing the last traces of this metal.

STAS has pointed out that the chloride may exist in any one of four different states, namely, gelatinous, curdy flocculent, pulverulent, or granulo-scaly-crystalline. These forms vary much as to their solubility in water. The second modification—obtained by precipitation from cold solutions—is the most soluble. Chloride of silver forms double salts with ammonium, barium, sodium, and osmium.

Silver Iodide, AgI, is precipitated upon adding hydrochloric acid, or a soluble iodide, to a solution of nitrate of silver, and occurs native as iodite. It is of a dingy yellow colour, with a density of 5·02, insoluble in water, and decomposed when heated with potash. Like the chloride, it is discoloured by light, and hence its use in DAGUERRE'S photographic process—the plate of silvered copper intended to receive the image in the camera being prepared by exposing it in a box containing iodine. The iodide is soluble in a hot solution of hydriodic acid or concentrated iodide of potassium, and is distinguished from the chloride, not only by its yellow colour, but also by its being almost insoluble in ammonia; this constitutes its special characteristic.

Silver Bromide, AgBr, is occasionally found native as bromite, and is prepared in a manner analogous to the iodide; its properties are also analogous, and both are soluble in hyposulphite of soda and employed in photography.

Silver Fluoride, AgF, is produced by dissolving monoxide or carbonate of silver in hydrofluoric acid. When iodine gas is passed over the fused crystals of this salt, chloride of silver is formed and fluorine set free. An oxyfluoride having the formula AgF,AgHO, also exists.

Silver Nitrate, $AgNO_3$, is the most important salt of this metal. Its density is 4·355, and it is obtained by dissolving silver in nitric acid diluted with 3 parts of water; nitric oxide is disengaged, and if the silver contain copper, the solution will have a bluish tinge; if gold, that metal will remain undissolved in the form of a black powder. The solution of nitrate of silver should be perfectly clear and colourless. It is caustic, and tinges animal substances of a deep yellow, which, by exposure to light, becomes a deep purple or black stain, and light appears only to be capable of decomposing it when in contact with organic matter. It is the essential ingredient in many of the washes employed for dyeing the hair, and in the so-called *indelible* inks for marking linen; but cyanide of potassium will remove the black stain produced by any of the preparations of silver. The crystals are colourless, transparent, anhydrous tables, soluble in an equal weight of cold, and in half their weight of boiling water. Alcohol also dissolves about one-fourth of its weight of this salt at its boiling point, but deposits nearly the whole as it cools. When heated in a silver crucible the nitrate fuses into a grey mass, and if cast into small cylinders forms the *lapis infernalis* or *lunar caustic* of the pharmacopœia. Ivory, marble, and several other bodies may be stained black, or even silvered, by soaking them in a solution of nitrate of silver, and fully exposing them to the action of the sun's rays. A plate of copper, introduced into a solution of this salt, occasions a brilliant precipitation of crystalline silver, and the copper is oxidised and dissolved by the acid. The introduction of mercury into the solution causes a beautiful crystalline deposit of silver, known as the *arbor Dianæ*. Hydrogen has a remarkable power of reducing this salt when in solution, and the metal so obtained is very pure. Nitrate of silver forms several double salts.

Silver Nitrite, $AgNO_2$, is obtained by causing nitrate of silver and an alkaline nitrite to react on each other. It crystallizes as long white needles, and is soluble in about 120 times its weight of cold water.

Silver Sulphide, Ag_2S, may be obtained by heating finely-divided silver, or plates of silver, with sulphur, and occurs abundantly in nature as silver glance. It is a grey crystallizable compound, considerably more fusible and much softer than silver, and having a density of 6·85. The presence of sulphuretted hydrogen in the air occasions the tarnish upon silver, which, though only superficial, is a great obstacle to many applications that might otherwise be made of this valuable metal; but in the process known as *niello* it is used, in conjunction with other metallic sulphides, for producing black designs on engraved silver. Silver which has been discoloured by the formation of sulphide may be at once restored to its original colour by heating in a solution of hameleon mineral (manganate of potash). It is insoluble in water, but dissolves in nitric acid with liberation of sulphur. It forms double sulphides with iron and copper.

Silver Sulphate, Ag_2SO_4, is deposited when sulphate of soda is mixed with nitrate of silver in solution. It is also formed by boiling silver with its weight of strong sulphuric acid. Upon the large scale, small portions of gold may be most economically separated from large quantities of silver by heating the finely-granulated alloy in sulphuric acid, in the manner described in the article on GOLD (see vol. ii. p. 92).

It is a white inodorous powder, soluble in 88 times its weight of boiling water, with a disagreeable metallic taste, and when exposed to light it gradually turns green. An acid sulphate, having the formula $AgHSO_4$, also exists as faintly yellow prisms, which crystallize out from a solution of the normal salt in less than 3 parts of sulphuric acid.

Silver Sulphite, Ag_2SO_3, is prepared by precipitating a silver salt by an alkaline sulphite, and crystallizes in white shining needles. It is very slightly soluble in water, and has a disagreeable taste.

Silver Thiosulphate is not known in a free state, but forms two series of double salts, having the formula $R_4Ag_2S_6O_9$ and $RAgS_2O_3$ (R indicating an alkaline metal). Those of the first class are easily soluble in water, while those of the second are very sparingly soluble in it, and these latter may be used for silvering purposes.

Silver Dithionate (*Hyposulphate*), $Ag_2S_2O_6 + 2H_2O$,

is formed when oxide or carbonate of silver is dissolved in dithionic acid.

Phosphates of Silver.—Three of these occur, namely:—(1.) Triphosphate, Ag_3PO_4, obtained by precipitating a solution of ordinary phosphate of soda by one of nitrate of silver; it is a yellow precipitate, which turns black on exposure to light. (2.) Pyrophosphate, $Ag_4P_2O_7$, is obtained in a similar manner, employing pyrophosphate of soda. (3.) Metaphosphate, $AgPO_3$, by using the metaphosphate of soda.

Silver Carbonate, Ag_2CO_3, is precipitated in the form of a white insoluble powder, by adding carbonate of potash to nitrate of silver. It blackens on exposure to light, and is easily decomposed by heat.

Silver Fulminate, $Ag_2Cy_2O_2$.—This curious and dangerous compound, used for making crackers and other detonating toys, is prepared as follows:—100 grains of fused and finely-powdered nitrate of silver are added to 1 oz. of warm alcohol, and the mixture stirred with a wooden stirrer in a sufficiently large glass basin; 1 oz. of fuming nitric acid is then added, when a violent effervescence ensues, and a powder is formed; after the liquid has cooled, this is collected upon a filter, washed, and carefully dried at a temperature not exceeding 100°. In collecting and handling this powder the utmost caution is requisite. It should be made in very small quantities only, and touched with nothing hard; for it has sometimes exploded upon the contact of a glass rod even under water. The feather of a common quill serves to collect it; and it should be kept in a wide-mouthed vessel covered by paper, and by no means in a stoppered or even a corked phial, as serious accidents have arisen from its unexpected explosion. It is deposited as small, white, opaque, shining needles, with a strong, bitterish, metallic taste, and very poisonous; and it is slightly soluble in cold water, and more freely in ammonia. It blackens on exposure to light, giving off carbonic acid and nitrogen. Gunpowder may be mixed with this compound, and when the fulminate is exploded the powder is, according to LIEBIG, scattered about, and not ignited. Many substances are capable of decomposing it, and an extensive series of double fulminates exists. It has been a subject of inquiry by many chemists, more especially GAY-LUSSAC and LIEBIG. The compounds of silver with manganic, chromic, molybdic, and other acids, are very numerous; but as they are unimportant, it will not be necessary further to refer to them.

ALLOYS OF SILVER.—The alloys of most importance in the arts are those which this metal forms with copper, copper and zinc, and copper, nickel, and zinc, as these are used for the subsidiary coinage in various countries; but it may be alloyed with most other metals. The presence of small quantities of some metals—such as antimony, arsenic, bismuth, tin, and zinc—renders silver brittle, and therefore unsuited to the purposes of coinage, &c.

Aluminium forms with silver alloys which are much harder than aluminium, but fuse at a lower temperature, and are therefore used as solder for it.

Copper alloys with silver in all proportions, and forms very ductile and elastic but hard alloys, which are capable of taking a brilliant polish. So long as the copper does not exceed about one-eighth of the silver, the alloy is white; but the surface is made white in the case of the poorer class of alloys by oxidising the superficial copper, and subsequently dissolving this oxide in hot dilute sulphuric acid. In France three standard alloys are employed, namely:—

95 per cent.	of silver	and	5 per cent.	of	copper	for medals and plate.
90	"	"	10	"	"	for coin.
80	"	"	20	"	"	for jewellery.

In Germany and Austria two standards, containing 90 and 87·5 per cent., are employed.

A curious phenomenon, known as liquation, takes place when alloys of silver and copper pass from the liquid to the solid state, whereby it is rendered impossible to obtain a perfectly uniform alloy of these two metals. LEVOL found that with alloys of a standard higher than that containing 71·9 per cent. of silver, the mass is richest in the centre, while with this alloy (in which the metals exist in the exact proportion represented by the formula, Ag_3Cu_2) no liquation takes place, and below this point the liquation renders the inside poorer in silver than the outside. ROBERTS finds, however, that these differences are very considerably modified according to the rate at which the mass is allowed to cool. The English standard alloy, containing 92·5 per cent. of silver, will be described subsequently.

Gold alloys with silver in all proportions, and the metals usually accompany each other in the native state. The manner in which gold is extracted from this alloy in a pure state has been already explained in the article on GOLD.

Lead, in very small quantities, forms a brittle alloy with silver. It is capable of alloying in any proportion, and forms, as already shown, a convenient medium for extracting silver from all oxidisable metals with which it may be alloyed.

Nickel forms a highly-magnetic alloy with silver, and that containing 10 per cent. of nickel is used for subsidiary coin in Switzerland.

Platinum and silver form a series of alloys, which are less ductile than pure silver. Even though the former metal be only present in very minute quantities, it prevents cupellation.

Palladium and *iridium* also form alloys with silver.

Zinc, in conjunction with copper, is alloyed with silver to form the metal which constitutes the subsidiary coins of France; the composition is given as—

	Parts.
Silver,	835
Copper,	93
Zinc,	72
	1000

And an alloy of 80 per cent. of silver and 20 per cent. of zinc constitutes DÖPPLER'S reflector metal.

With *mercury* silver readily amalgamates. When red-hot silver is thrown into heated mercury, it

dissolves; and when 8 parts of mercury and 1 of silver are thus combined, a granular crystalline soft amalgam is obtained, the density of which exceeds the mean density. When a solution of this amalgam in mercury is squeezed through chamois leather, the excess of mercury, carrying along with it only a small portion of silver, goes through, and the solid amalgam is left behind.

BERZELIUS found a crystalline amalgam to contain 65 per cent. of mercury and 35 per cent. of silver. Silver amalgam may be employed for plating copper or brass with a coating of silver by simply covering the metal (previously cleaned) with the amalgam, and applying heat; but the process cannot be advocated, and the methods subsequently referred to are preferable.

Standard Silver.—In England the same alloy is employed both for the coinage and for the manufacture of plate, and it has been in use from the earliest times. It contains 11 ozs. 2 dwts. of silver and 18 dwts. of copper per troy pound—*i.e.*, 92·5 per cent. of the former and 7·5 per cent. of the latter metal—and is known as "standard" silver. A richer alloy, containing 95 per cent. of silver, is employed for the manufacture of medals. The density of the standard metal is lower than calculation would indicate, being only 10·20 instead of 10·35.

In order that the standard of plate may be maintained, the Goldsmith's Company in London, and the assay offices in several of the larger towns, are required to impress on all plate, as in the case of gold, before it is offered for sale, a mark to indicate that it is of the requisite standard, together with certain other marks indicating the date, the maker's name, and the payment of duty; the expense of such examination being defrayed by the manufacturer.

When silver alloyed with copper, such as standard silver, is exposed to a red heat in the air, it becomes black from the formation of a superficial film of oxide of copper. This may be removed by immersion in hot dilute sulphuric acid, and a film of pure silver then remains, of a beautiful whiteness; this is called *blanched*, or *dead silver*. It is usual to employ this process in order to improve the colour of objects formed of alloyed silver; the article, when heated nearly to redness, is plunged, while still hot, into water acidulated either with nitric or sulphuric acid; the external oxide of copper is thus entirely removed; and the matted appearance of the pure silver, which now forms the surface, soon gives place to a bright polish by rubbing with a burnisher. The blanks for coin may be treated in this way before they are struck; but the practice was abolished in the English Mint for reasons already given in the account of the coinage contained in the Article GOLD, see page 102.

Articles of plate are often deadened or matted by boiling in bisulphate of potash, which acts in the same way as the dilute sulphuric or nitric acid.

Silver Solder consists of—

Silver,	667
Copper,	233
Zinc,	100

Spectrum of Silver.—The spectrum of silver contains twenty-five lines; of these, two, situated in the green, exceed in brilliancy the well-known sodium lines in the yellow, and all the important silver lines are in the same green portion of the spectrum. The absorption spectrum, produced by the vapour of silver obtained in the manner adopted by M. STAS, was found by LOCKYER and ROBERTS to belong to the class denominated by the former channel-spaced spectra.

SILVERING.—Almost all kinds of silvering are now performed by electro-chemical deposition, and for full details of the process the reader is referred to the article ELECTRO-METALLURGY; but it will be necessary here to enumerate certain processes by which silver can be deposited on various substances without the aid of the voltaic current. The coating of the backs of ordinary mirrors and looking-glasses consists of an amalgam of tin and mercury; a coating of real silver may, however, be deposited on glass by one of the methods subsequently enumerated.

Silver-plating, properly so called, consists in causing a thin leaf of this metal—prepared by hammering in the manner already described in detail in the article on GOLD (see vol. ii. p. 103)—to adhere firmly to the surface of another metal, always of course of an inferior value. When silver-leaf is to be applied to the surfaces of bodies, the methods prescribed for gold-leaf are also generally suitable. Among the metals, copper, brass, and German silver are those on which the silverer most commonly operates; iron is seldom silvered, but the process is essentially the same. The principal steps of the operation are summarily described by Dr. URE as follows:—

1. The *smoothing down* the sharp edges, and polishing the surface of the copper, or other metal, to be silvered.

2. The *annealing*, or making the piece to be silvered red-hot, and then plunging it in very dilute nitric acid, till it is bright and clean.

3. *Pumicing*, or clearing up the surface with pumice-stone and water.

4. The *warming* to such a degree merely as, when it touches water, it may make a hissing sound; in this state it is dipped in very weak aquafortis, whereby it is roughened sufficiently to retain the silver leaves that are to be applied.

5. The *hatching*.—When the asperities so formed are inadequate for giving due solidity to the silvering, the plane surface must be hatched all over with a graving tool; but the chased surfaces need not be touched.

7. The *charging*, the workman's term for silvering.—This operation consists in placing the silver leaves on the heated piece, and fixing them to its surface by burnishers of steel of various forms. The workman begins by applying the leaves double. Should any part darken in the heating, it must be cleared up by the scratch-brush.

After applying two silver leaves, he heats the articles to the same degree as at first, and then fixes on with the burnisher four additional leaves of silver; and he

goes on *charging* in the same way four or six leaves at a time, till he has applied, one over another, thirty, forty, fifty, or sixty leaves, according to the desired solidity of the silvering. He then burnishes down with great pressure and address, till he has given the surface a uniform silvery aspect.

Silvering by the aid of heat may be performed in various ways, of which the following are the most important:—The surface, previously cleaned with care, and dipped in a solution of nitrate of mercury, is covered with a uniform layer of silver amalgam, and subsequently heated, first gently, and when the layer is found to be uniform, the heat is raised to expel the mercury, and the surface is subsequently burnished.

A mixture consisting of 1 part of silver in a fine state of subdivision, 4 of sal-ammoniac, 4 of common salt, and one-fourth part of corrosive sublimate, is made and formed into a paste, with a sufficient quantity of water; and when the surface of the article has been coated with this mixture, it is heated to the fusing point of the mixture of salt.

Another method consists in rubbing the surface with a mixture of equal parts of chloride of silver, silver in a fine state of subdivision, and calcined borax, heating to a dull redness, and then introducing the article into a solution of common salt and cream of tartar; then covering the surface with a paste of equal parts of sal-ammoniac, common salt, and sulphate of zinc, again heating and dipping into the same liquid. This process is repeated until a surface of the requisite thickness is obtained.

Silvering without the aid of heat, and by Immersion.—The following are a few of the preparations and solutions which have been recommended by various authors as suitable for depositing silver without the necessity of raising the temperature of the body—a practice which would in many cases destroy the article by fusing the soldered joints:—

The old method of obtaining a thin coat of silver consisted in employing a paste formed by mixing water with equal parts of chalk, cream of tartar, and chloride of silver; or with 1 part of freshly precipitated chloride of silver, 5 of common salt, and 5 of cream of tartar.

A second process, recommended by Roseleur and Lanaux, is to dissolve 6 parts of sulphite of soda and 1 part of a salt of silver in 6 parts of water, the object being warmed after rubbing with this mixture.

Another method—frequently adopted for plating small brass or copper articles, such as the scales of thermometers—consists in rubbing them, after being properly cleaned, with a mixture of 100 parts of cream of tartar, 10 of chloride of silver, and 1 of corrosive sublimate: the surface should then be polished.

If a wet rag be dipped in a powder consisting of 2 parts of cyanide of potassium, 1 of nitrate of silver, and 5 of chalk, and rubbed on the surface of an object, it is, according to Boudier, covered with a firmly adhering layer of silver.

Silvering of Glass, &c.—Drayton proposed in 1843 a method of coating glass surfaces, such as mirrors, &c., by the reduction of an ammoniacal solution of nitrate of silver by one of the essential oils.

The process, as modified by Petitjean, is carried out as follows:—The glass to be silvered having been laid on a horizontal cast-iron table, is well cleaned, and solutions of the silver salt and tartaric acid are poured over it. In twenty minutes the deposition commences, and the whole process is completed in an hour and a quarter. The liquid is now poured off, and the glass washed, dried, and covered with a coat of varnish. The deposition by this means has the advantage of being a perfectly healthy occupation, and costing less than when mercury is employed; but the method, nevertheless, has certain objections, the principal of which is a yellowish tint on the glass; but all of them are effectually avoided by the modification introduced by Lenoir, which consists in sprinkling the surface after washing with a dilute solution of the double cyanide of mercury and potassium. The silver is partially dissolved, while an amalgam is instantaneously produced, both more adhesive and much whiter than pure silver. The solar rays, moreover, have less effect upon it than before such a treatment, neither are sulphur vapours so liable to attack it.

Estimation of Silver.—The behaviour of various reagents with solutions of silver is given in a tabular form in the article on Gold, to which the reader is referred. In general, the *soluble* salts of silver are recognized by furnishing a white precipitate with hydrochloric acid and the soluble chlorides, which blackens by exposure to light, and which is readily soluble in ammonia; and by affording metallic silver upon the immersion of a plate of copper. The salts *insoluble in water* are mostly soluble in ammonia; and when heated with carbonate of soda on charcoal before the blow-pipe they afford a globule of silver. A yellow precipitate on the addition of phosphate of soda to a neutral solution, a red-brown with arseniates, a crimson with the chromates, and white with ferrocyanide of potassium, are further characteristics of the soluble salts of silver.

Tin and lead are the most rapid precipitants of metallic silver from the nitrate; cadmium, zinc, copper, bismuth, and antimony are more slow in their operation, and mercury still more tardy. Chloride of silver is rapidly reduced by most of the metals which form soluble chlorides, such as zinc, iron, cadmium, cobalt, and arsenic. Zinc, copper, and arsenic rapidly reduce the ammoniacal solution of oxide of silver. Of all the metallic precipitants zinc and cadmium are the most effective; when zinc or antimony is used, the separated silver contains the precipitating metals.

The solubility of silver in nitric acid, and the complete insolubility of its chloride in acid solutions, facilitate the separation of silver from other metals. When its amount is to be estimated quantitatively, the alloy or pulverized ore is dissolved in nitric acid, and the silver is precipitated as a chloride by adding a slight excess of hydrochloric acid. In order that a dense precipitate may be obtained, the solution should be heated nearly to

the boiling point previous to the addition of the precipitant. When the whole of the chloride has settled at the bottom of the vessel, the supernatant liquor is carefully drawn off by means of a glass syphon; and the chloride, after being well washed by repeated decantations with water slightly acidulated with nitric acid, is transferred to a thin porcelain capsule, the weight of which has been accurately ascertained. It is carefully dried in a water bath, and then heated over the flame of a gas-burner or spirit lamp until it fuses, and the crucible with its contents are again weighed while warm. The difference between the first and second weighings gives the amount of the chloride, from which that of the silver can be deduced by the simple proportion:—

As 100 : 75·27 : : K, or the weight of chloride obtained, to x, the weight of silver in the ore operated on; since every 100 parts of the chloride correspond to 75·27 parts of metallic silver.

This principle is applied to the assay of bullion in the Indian mints, and will be found referred to under the head, "Humid Methods of Assay," at page 760.

Valuation of Silver Alloys.—In the article on Gold (vol. ii. page 96) it has already been explained that silver assays may be reported either on the French or decimal system, or on what is called the trade system. On this latter the assay pound (usually 12 grains troy) is divided into 12 parts called "ounces," each "ounce" into 20 "pennyweights," and each "pennyweight" into 24 "excess grains." Thus the whole assay pound contains 5760 excess grains, and the division is exactly analogous to that of the troy pound; any report, therefore, on this system gives at once, without calculation, the amount of fine silver per troy pound of the alloy. The following tables, similar in form to those given in the *Valuation of Gold Alloys*, will be found useful:—

Ounces.	Decimal Equivalent.	Pennyweights.	Decimal Equivalent.	Excess Grains.	Decimal Equivalent.
1	83·3̇	1	4·16̇	1	0·17361̇
		2	8·3̇	2	0·3472̇
2	166·6̇	3	12·49̇	3	0·52083̇
		4	16·6̇	4	0·694̇
3	250·0	5	20·83̇	5	0·86805̇
		6	24·9̇	6	1·0416̇
4	333·3̇	7	29·16̇	7	1·21527̇
		8	33·3̇	8	1·38̇
5	416·6̇	9	37·49̇	9	1·56249̇
		10	41·6̇	10	1·7361̇
6	500·0	11	45·82̇	11	1·90972̇
		12	49·9̇	12	2·083̇
7	583·3̇	13	54·16̇	13	2·25694̇
		14	58·3̇	14	2·4305̇
8	666·6̇	15	62·49̇	15	2·60416̇
		16	66·6̇	16	2·7̇
9	750·0	17	70·83̇	17	2·95138̇
		18	74·9̇	18	3·1249̇
10	833·3̇	19	79·16̇	19	3·29861̇
		20	83·3̇	20	3·472̇
11	916·6̇			21	3·64583̇
				22	3·8194̇
12	1000·0			23	3·99305̇
				24	4·16̇

Assay Pound.	Ounces.	Pennyweights.	Excess Grains.	Decimal Equivalent.
			1	0·1736
		1	24	4·13̇
	1	20	480	83·6̇
1	12	240	5760	1000·0

The terms betterness and worseness (indicated by B and W) are used to show that the alloy contains a greater or less proportion of the precious metal than the standard alloy, which contains $\frac{925}{1000}$, or 11 ozs. 2 dwts. per lb. troy. Excess grains, however, whether used in conjunction with B or W, always express betterness. Thus a report, B, 6½ dwts. 5 excess grains, would indicate an alloy containing 5 grains per lb. of silver more than that contained in an alloy of the standard, B, 6½ dwts.; and further, a report, W, 6½ dwts. 5 excess grains, would not indicate an alloy containing 5 grains per lb. *less* than the report, W, 6½ dwts., but this amount in excess of that report. This difference will be more clear if the decimal equivalents be given:—

Trade Report.	Decimal Equivalent.
B, 6½ 5,	952·95
B, 6½ 0,	952·08
W, 6½ 5,	898·82
W, 6½ 0,	897·95

Assay of the Alloys and Ores of Silver in the Dry Way.—In this process the object sought is to obtain the silver and other metals that may be present in the form of an alloy with lead, which is afterwards introduced into the muffle, and cupelled in the ordinary way. All the oxidisable metals are thus removed, the silver remaining behind in a pure state—that is, free from all metals except gold, platinum, and any other non-oxidisable metals that may be present. Should appreciable quantities of such metals be known to be present, the dry method of assay is not applicable in its simple form, but must be supplemented by the use of nitric acid, as described under the heading, "Parting Assays," in the assay of gold (vol. ii. page 122); or one of the wet methods of assay of silver, subsequently described, may be resorted to.

The preliminary operations to which minerals containing silver are subjected, and the form of the cupels and other apparatus employed, have been fully described in connection with the analogous processes followed in the assaying of gold ores, and therefore it will be quite unnecessary to repeat them in this place.

Ores, according to their nature, are either (1) fused with a reducing flux, such as charcoal or black flux in conjunction with litharge, in order to produce metallic lead in which to collect the silver; or (2) fused with an oxidising agent, such as litharge or nitre; or (3) scorified.

Ores of silver, in which the metals that are present exist in the form of reducible oxides, are commonly treated according to the first of these methods. The proportion of litharge employed for this purpose, says Phillips, must be varied according to circum-

stances, as the resulting button of alloy should not be too rich, since in that case a portion of the silver is lost in the slag; nor too poor, as the cupellation would then occupy a long time, and a loss through sublimation be entailed. In ordinary cases, if 400 grains of ore be the quantity operated on, a button of 200 grains will be a very convenient amount for cupellation; and this may be obtained by the addition of 300 grains of litharge, and from 7 to 8 grains of finely-powdered charcoal. The whole is to be well mixed with 200 grains of carbonate of soda on a sheet of highly-glazed paper, and afterwards introduced into an earthen crucible, of which it should not fill more than two-thirds the capacity. It is now covered with a thin layer of borax, and heated in an ordinary assay furnace—care being taken to withdraw it from the fire as soon as a liquid and perfectly homogeneous slag has been obtained, as the unreduced litharge would otherwise be liable to eat through the pot and spoil the experiment. When it has sufficiently cooled, the crucible is broken, and the button of alloy obtained is cupelled. When other minerals than oxides or carbonates are to be examined, the addition of charcoal, or any similar reducing agent, becomes in many instances unnecessary, as litharge readily attacks all the sulphides, arsenio-sulphides, &c., and oxidises nearly the whole of their constituents, with the exception of silver, whilst a proportionate quantity of metallic lead is at the same time set free. The slags formed in this way contain the whole of the excess of litharge added, and the button of alloy produced is subjected to cupellation in the usual manner.

All the directions given with regard to the assay of gold ores (see vol. ii. page 114), and the method there described for diminishing the amount of reduced lead which has to be subsequently treated by cupellation, apply with equal force to the assay of silver ores, and need not here be repeated. The treatment to which an ore is subjected depending to a great extent on its nature, it is well to make a preliminary assay, in order that in the actual assay only a certain amount of lead alloy may be submitted to cupellation. Mitchell recommends that all ores be subdivided into three classes, indicating the special treatment to which they should be subjected. These classes are—(1) Ores which, on fusion with excess of litharge, give no metallic lead, or less than their own weight. (2) Those which give their own weight, or nearly so, of metallic lead; and (3) those which give more than their own weight of metallic lead. For this preliminary assay 20 grains of very finely pulverized ore are mixed with 500 grains of litharge, and placed in a crucible of such size that it is only half full. After being carefully warmed it is rapidly heated in a bright fire, and when the mixture is thoroughly fused the pot is removed, cooled, and broken. The ore belongs to the first, second, or third of the above classes, according as the resulting button weighs less than, the same as, or more than 20 grains, the weight of ore originally taken. Now 200 grains of lead alloy is a convenient quantity to cupel; hence, in the actual assay, bodies of the second class require simple fusion with litharge and a suitable flux; those of the first class require the addition of such a quantity of a reducing agent that the final button may weigh 200 grains; and those of the third class, such a proportion of an oxidising agent as shall oxidise all lead in excess of 200 grains. An excellent reducing agent is argol (commercial cream of tartar); and nitrate of potash is the oxidising agent usually employed. The former is capable of reducing about 6 times its weight of litharge, and the latter of oxidising about 4 times its weight. These data suffice for determining the quantities required for assaying ores of the first and third classes respectively, when the results of the preliminary assays are known.

Scorification.—This process has been sufficiently described under the *Assay of Gold:* it is only necessary to add that it is applicable to every kind of argentiferous matter, and is both the most convenient and the most exact method of assay when large numbers of assays are required to be done.

Cupellation.—This process has also been described in considerable detail in the *Assay of Gold;* but it will be necessary here to give some account of the precautions to be taken when silver is under examination.

In the assay of alloys of silver with copper it is, of course, necessary to add the requisite amount of lead; whereas when ores are being assayed, the preliminary fusion or scorification has rendered this unnecessary. If the composition of an alloy be not approximately known, a preliminary assay will therefore be needed. An experienced assayer will frequently be able to judge with sufficient accuracy from the colour and hardness of the metal; but when cupellation must be resorted to, 50 grains of pure lead and 2 grains of the alloy may be introduced into the cupel, and worked in the manner about to be described. Or the composition may be roughly ascertained by comparing the appearance of a streak made by the alloy on a touchstone with those of a series of "test needles," or by noting the amount of oxidation produced on a clean piece of the alloy when introduced into the muffle for a definite period. Gay-Lussac himself suggested that a galvanic couple, formed of the unknown alloy and pure silver, should be employed as a means of determining its approximate composition; or else, that a series of standard alloys be used, and successively associated with the alloy until no deflection of the galvanometer needle is observed.

The amount of lead present should be greater in proportion as the quantity of copper is more considerable; but in cupelling an alloy of silver and copper, the same amount of lead cannot safely be added as in treating an alloy of copper and gold, as the greater volatility of the silver would cause a considerable loss of that metal before the whole of the lead could be absorbed. In this case, therefore, the following table, showing, according to D'Arcet, the amount of lead necessary to effect the proper cupellation of various alloys of silver and copper, must be substituted for that given at the place above referred to:—

Standard of Silver.	Ratio of Weight of Lead to Weight of Assay.	Ratio of Weight of Lead to Weight of Copper Present.
1000	3-10th to 1	—
950	3 to 1	60 to 1
900	7 to 1	70 to 1
800	10 to 1	50 to 1
700	12 to 1	40 to 1
600	14 to 1	35 to 1
500	16 or 17 to 1	32 or 34 to 1
400	16 or 17 to 1	27 or 28 to 1
300	16 or 17 to 1	23 or 24 to 1
200	16 or 17 to 1	20 or 21 to 1
100	16 or 17 to 1	18 or 19 to 1
Pure copper.	16 or 17 to 1	16 or 17 to 1

Makins, however, points out that there are great difficulties in working fine silver with less than three times its weight of lead, and he considers that results obtained on alloys very rich in silver are not satisfactory when a smaller quantity is used. He employs six times its weight for the assay of metal of the English standard (925 parts to 1000), and increases the proportion for coarser varieties.

In the above table the numbers in the second column, which express the quantity of lead necessary to be added in each case, are multiples of the weight of alloy on which the operation is performed. Hence, in the third line, for example, in which the alloy consists of 900 of silver and 100 of copper for each grain of alloy taken, 7 grains of lead will be necessary; and as each grain of alloy contains only one-tenth of its weight in copper, it follows that the ratio of the lead to the copper is as 70 to 1.

It will be remarked also that here, as in the table given for an alloy of gold and copper, the proportion of lead to be employed for a silver alloy below the standard of 500 remains constantly the same.

Although silver is not appreciably volatilized when melted alone, yet it is so to a certain extent in the presence of lead, and therefore the cupellation should be made at the lowest temperature at which the absorption of the litharge can be effected; and even when every precaution is used, there is always a loss of silver in cupellation, for which allowance must be made.

It must be carefully noted, however, that the heat must be raised as much as possible, in consequence of the necessity of removing *all* foreign metals on the cupel—the furnace process not being followed, as in the case of gold, by treatment of the button in nitric acid. The cooling also of the furnace must be accomplished with considerable care, in order to avoid loss of silver by the expulsion of oxygen, which attends the rapid solidification of silver buttons. The heat should therefore be so adjusted that only slight fumes are visible over the cupels, and the fused metal should be very luminous and easily distinguishable from the cupel. With too low a temperature, crystals of litharge are liable to collect round the button; and with an excessive heat, the fumes rise rapidly to the crown of the muffle. In cooling down the furnace prior to withdrawing the assays, special care must be taken to avoid the admission of cold air into the muffle, as this would be followed by the "spitting" mentioned above. A convenient method of avoiding such an accident consists in surrounding the closed door of the muffle with glowing coals, and in not opening it until the upper coals in the furnace are black.

When other metals besides lead and silver are present in an alloy, the cupel usually affords indications, from which it is generally possible to judge of their nature, and roughly of the amount in which they exist.

The following are the results of experiments made in order to ascertain the influence of the several metals on the nature of the resulting button, and the action on the cupel; but the appearance due to each metal is so often masked by the presence of another, that the indications given cannot be considered of much practical value:—

Aluminium.—Yellowish stain, with scoria which float on the surface of the button.

Antimony.—Light yellow slag, which sometimes cracks the cupel.

Arsenic.—Sage green stain.

Cadmium.—Black ring near the top of the cupel.

Chromium.—Dark brick-red stain.

Cobalt.—Dark green scoria and greenish stain.

Copper.—Dark brown or green colour.

Iron.—Dark red-brown stain at commencement of operation, leaving a dark ring on the cupel.

Lead.—Straw or orange-yellow colour.

Manganese.—Dark bluish-black stain and corrosion of the cupel.

Nickel.—Dark green scoria and greenish stains.

Palladium and Platinum.—Green stain and very crystalline button.

Tin.—Forms a grey slag.

Zinc.—Yellow ring on cupel; the metal burns with a brilliant flame, gives out copious vapours, and corrodes the cupel.

On withdrawing from the muffle, the buttons are usually struck on their sides, on an anvil, prior to brushing them with a stiff brush, in order to remove all adhering bone-ash, when they are ready for weighing. The loss by volatilization and absorption in the cupel being much greater than in the assay of gold, it is usual in works on assaying to give a table exhibiting the results of experiments made in the French Mint, with a view to ascertain the amount of such loss in alloys of all degrees of fineness. Such a table is, however, of but little use to the assayer, as the loss depends on so many varying circumstances that it is far from being *constant*, even when every precaution is taken. The best method of eliminating it is the use of a number of "check" assays made on fine silver, side by side with the metal under examination, in the manner recommended in the article on the assay of gold. Since, however, the loss is much greater, and varies considerably throughout the muffle, it is necessary that a greater number of check assays be made. In the Royal Mint nine checks are worked in a fire of 45 assays, or one in each row, and a correction is applied to each assay deduced from the checks in its immediate neighbourhood. Considerable judgment is required in applying such corrections to the weights obtained.

The amount of the correction may be as much as 10 parts in 1000, and the experiments of Hambly appear to show that the loss of silver increases with the weight of lead present.

Other Methods of Estimating Silver in the Dry Way:—The two following processes for determining the amount of silver without first dissolving it are described by Fresenius, and are applicable in the cases specified:—

(1) *Determination as Chloride.*—Specially applicable to bromides and iodides of silver. The mass under examination is placed in a bulb tube, and after fusion is cooled and weighed. Chlorine gas is then caused to pass over for some time, the bulb being weighed from time to time until no change of weight is observed; care must be taken to remove any residual chlorine gas before weighing.

(2) *Determination as Metallic Silver.*—Applicable to oxide and carbonate of silver, its compounds with organic acids, and its chloride, bromide, and sulphide. In the case of oxides, carbonates, and compounds with organic acids, a simple ignition in a porcelain crucible will suffice. The results can be taken to be absolutely accurate, except when organic salts are examined, when there is a chance of a minute quantity of carbon being retained in the silver. For the estimating of chlorides, bromides, and sulphides (but not iodides), the apparatus used for determining as chloride may be used, hydrogen gas being substituted for chlorine.

Humid Methods of Assay.—Various methods have been proposed from time to time for estimating the amount of silver contained in a solution of this metal; in some of these the precipitate is dried and weighed, and the amount of silver present determined by calculation, and in others the volumetric method is resorted to. Fresenius classifies the first series as follows:—

(1) *Chloride of Silver.*—This method is applicable to all compounds of silver. It has been already briefly referred to; but it may be well to describe in a few words the system now practised in the Indian Mints, where it is exclusively employed for the assay of silver bullion.

After the samples of alloy for assay have been accurately weighed, so that each weighs 18·817 grains (for a reason that will presently appear), they are transferred to 12-ounce stoppered bottles, and to each is added 1·5 drachm of nitric acid of specific gravity 1·200 for ordinary standard metal (that is, containing 916·6 parts per 1000, which is the standard of the Indian coinage), or 1·320 for fine metal, or when the nature of the alloy is uncertain; the solution is aided by a gentle heat. About 6 ozs. of distilled water and 1·5 drachm of hydrochloric acid, of specific gravity 1·060, are added to each bottle. They are well shaken, filled with water, and allowed to rest for four hours. The supernatant liquid is then carefully decanted by means of a syphon, and the chloride washed several times in distilled water. It is then transferred, under water, to a Wedgewood cup, in which it is broken up by a glass rod and dried at a moderate temperature, when it assumes a compact form, and should be transferred at once to the balance to be weighed while warm.

The weight of silver present can be deduced from the weight of chloride obtained, for each 100 parts of the latter contain 75·27 parts of fine metal; and the weight taken, 18·817 grains, is such that it would, if pure silver, produce exactly 25 grains of chloride. Thus, a decimal series of weights is prepared in which the 1000 weighs 25 grains; and if these be employed in weighing the chloride obtained, they will indicate the standard of the alloy without calculation. Chloride of silver, although extremely insoluble in water and dilute nitric acid, is soluble perceptibly in strong nitric acid and in hydrochloric acid, especially if concentrated and boiling. It is also soluble in most aqueous solutions of chlorides, and in solutions of the nitrates of the alkalies and the alkaline earths. Hence the method is specially applicable when none of these salts are liable to be present.

(2) *Sulphide of Silver.*—Sulphuretted hydrogen or sulphide of ammonium may be employed to separate silver—the former from any solution whatever, and the latter only from neutral and alkaline solutions. The precipitate is allowed to settle, filtered rapidly with the exclusion of air, and dried on a weighed filter at 100° C. There is a certain amount of risk, however, in the process, in consequence of sulphur being rapidly liberated if the sulphide be exposed to air, or if the solution contains substances which reduce sulphuretted hydrogen. When this seems probable, Rose recommends that it be converted into metallic silver by heating to redness in a porcelain crucible in a stream of hydrogen.

(3) *Cyanide of Silver.*—A neutral solution of silver is mixed with cyanide of potassium until the precipitate formed is dissolved; then nitric acid is added, and heat applied. Any free acid present must be neutralized. The precipitate is collected on a weighed filter, dried at 100° C., and weighed.

(4) *Metallic Silver.*—When nitric acid is present sulphuric acid is added, and the liquid evaporated till all the former is driven off; the sulphate formed is dissolved in hot water, and placed in a weighed porcelain crucible, in which is also placed a rod of cadmium. The silver is soon reduced; it is separated from the cadmium, and warmed with the acid fluid till no more hydrogen escapes, then washed, dried, ignited, and weighed.

Volumetric Methods of Assay.—The first of these introduced was that proposed by Gay-Lussac in 1832, and it is still largely practised, especially in mints, and wherever frequent assays have to be made on metal of nearly uniform composition. It will be necessary to describe it in some detail. After this some account will be given of other methods which have been proposed.

Gay-Lussac's Method.—It is based on the fact that hydrochloric acid and soluble chlorides are capable of completely precipitating silver from its solution in nitric acid, without acting on any other metal with which it may be associated, except mercury:

the presence of this metal can be at once ascertained in the manner subsequently described (see page 762), and any error which it would occasion may also be avoided.

The process might be conducted in either of the three following ways: — (1) By precipitating the silver by an excess of the chloride, and calculating the weight of metal from that of the chloride produced. (2) By determining the *weight* of a standard solution of salt which is required to precipitate the silver present. (3) By determining the *volume* of a standard solution of salt which is required for that purpose.

Of these the first is that employed in the Indian mints, which has been already referred to; the second is tedious, requiring considerable care, and is therefore rarely practised; and the third is that recommended by Gay-Lussac, which we now proceed to describe.

If the approximate assay of the alloy under examination be not known, it must be ascertained by one of the methods explained at page 758; or, if it be preferred, by the volumetric method described at the end of this article (see page 763). Such a portion of the silver alloy is taken as that it shall contain rather more than 1 gram. of pure silver; this amount is ascertained by the simple proportion,

$$A : 1000 : : 1{\cdot}0 : x,$$

where A is the approximate assay expressed in thousandths, and x the amount of alloy required, $\therefore x = \frac{1000}{A}$ grams.

The metal is dissolved in about 1 oz. of nitric acid, of specific gravity 1·190, by the aid of a gentle heat, and 100 c.c. of a standard solution of salt are added; this solution being of such a strength that 100 c.c. exactly precipitate 1 gram. of pure silver. The bottle is now shaken, either by hand or in the "agitator" shown in Fig. 14, in order to agglomerate the precipitated chloride of silver, and leave the supernatant liquid clear. Now, if the addition of a drop of salt solution to this liquid produces a precipitate, it will of course indicate that nitrate of silver still exists in the solution; but if no precipitate is formed, and a drop of a solution of nitrate of silver produces a precipitate, it is evident that too much salt has been added. Two drops of the above "normal" solution of salt suffice to deposit 1 milligram. of silver; hence, for delicate assays, it is usual to prepare a solution of one-tenth the strength, and to continue adding this, in c.c.'s at a time, until no further precipitate is obtained. The amount of salt so added (making an appropriate deduction where it has been found necessary to add silver, which is done by the aid of a titrated solution of the nitrate containing 1 gram. of pure silver in 1 litre of water) gives the requisite data for ascertaining the actual amount of silver present in the portion (x) of alloy taken for assay; whence the amount per 1000 parts may be ascertained by means of tables prepared for the purpose, or by the following simple proportion:—

$$x : 1000 : : M : S.$$

where x means the same as in the last case, M the amount of silver it contains, measured directly by the amount of salt added, and S the standard of the alloy, expressed in thousandths, $\therefore S = \frac{1000 \times M}{x}$.

The method, so far, is only capable of indicating the amount of silver present to the $\frac{1}{1000}$th part, but a skilled assayer can attain to even greater accuracy, for he will know by practice, from the amount of the precipitate obtained on adding a c.c. of the decimal solution of salt, whether, after shaking the liquid, a precipitate will be produced when a fresh addition is made; and therefore, knowing the amount produced when the solution is *just* saturated, he can estimate with the eye the fractional part of a thousandth, which any less precipitate proves to be present. The composition can thus be ascertained with considerable certainty to the $\frac{1}{10,000}$th part.

From the above brief account of the process it will be seen that three solutions are necessary, as well as suitable pipettes for the exact admeasurement of them. The solutions are—

(*a*) A standard or normal solution of salt.

(*b*) A decimal solution of salt.

(*c*) A decimal solution of nitrate of silver.

The preparation of these will now be described.

(*a*) The standard solution may be made either by adding a known weight of pure, thoroughly dry salt to a definite bulk of water, or, what is more convenient, especially where a large quantity of the solution has to be prepared, by diluting a saturated solution of salt to the requisite strength. To obtain pure chloride of sodium when the first method is adopted, a concentrated solution of the best table salt is treated with caustic baryta, to remove sulphuric acid and magnesia; then with a slight excess of carbonate of soda, to remove baryta and lime. The liquid having been warmed, any precipitate formed is allowed to subside. The supernatant liquid is evaporated, and the resulting crystals washed slightly, and carefully heated to dull redness. They may be kept in a glass-stoppered bottle. If attainable, chemically pure rock salt may be used in place of the above.

The atomic weights of silver and chlorine being, according to Stas, 107·929 and 35·457, it will be evident that 107·929 grams. of pure silver require for their complete precipitation as chloride, 35·457 grams. of chlorine; hence each gram. of silver requires 0·3285 gram. of chlorine, an amount which is contained in 0·54162 gram. of pure salt. If therefore it be required to prepare M litres of standard solution (an amount which will suffice for 10 × M assays), it will only be necessary to dissolve 5·4162 × M grams. of the pure salt in M litres of distilled water, care being taken that the solution is complete.

It is, however, more convenient to employ a saturated solution of salt, and common water, which, of course, itself contains a small quantity of salt, may be added to this until the requisite strength is attained. It is impossible to give the exact proportions necessary; but if the solution be thoroughly saturated, by being left to stand for a few days at a temperature of 15° C., the addition of 3 troy ozs. of

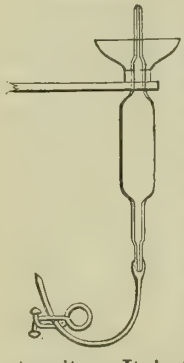
the saturated solution to each gallon of common water will give approximately the requisite strength, and further adjustment must be made after an assay on pure silver has shown the condition of the liquid.

(*b*) The decimal salt solution may be easily prepared by introducing 100 c.c. of the normal solution, by means of the pipette subsequently described, into a litre flask, and diluting the whole to 1 litre.

(*c*) For the decimal solution of silver, 1 gram. of chemically pure silver, prepared by one of the methods already described, is dissolved in a small quantity of pure nitric acid, and the liquid diluted to 1 litre.

The necessary apparatus is extremely simple, consisting principally of a pipette capable of accurately measuring 100 c.c. of liquid; tube pipettes, graduated in c.c.s, and having a fine opening at the lower end; and bottles, holding about 10 ozs., with carefully ground stoppers. The 100 c.c pipette, originally recommended by Gay-Lussac, is rarely, if ever, employed at the present day. Its use involved the careful adjusting of the level of the liquid to a graduation on a fine tube, and was thus liable to introduce considerable error in the results obtained. An excellent and extremely simple form of pipette has been proposed by Stas, which renders all adjustment by the eye unnecessary, and when carefully made it gives very accurate results. It is shown, accompanied by the necessary accessories, in Fig. 13, from which it will be seen that both ends are drawn out to a fine opening, which is about 0·09 inch in diameter at the lower extremity, and 0·04 inch at the upper extremity. It is found that if care be taken in grinding, the drop of liquid retained at the lower end is of a constant magnitude, and thus the amount delivered by the pipette is invariable.

Fig. 13.

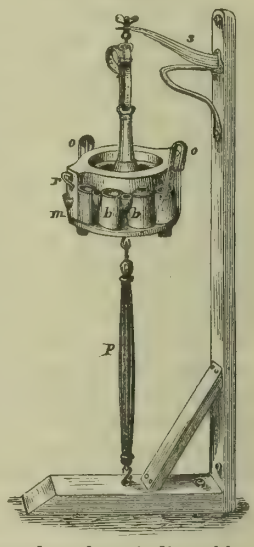


The solution is introduced at the lower extremity by means of an india-rubber tube connected with a large vessel, which is placed at an elevation above the level of the pipette. A perforated glass dish is affixed to the upper extremity, to collect any liquid which may escape at the opening; and when the pipette is full, the flexible tube is closed by a tap or a spring clip, the finger is placed on the upper opening, and the tube removed. When the lower portion of the pipette has been wiped, by drawing the fingers over it, the bottle is placed below, and the upper end opened by sliding the finger off—a motion which insures the same amount being always left within the tube.

The pipette employed for the decimal solution is a simple glass tube, about 10 inches in length and 0·35 inch in diameter, graduated in c.c.s, and terminating in a fine opening at its lower end. An arrangement for more delicately measuring small quantities of this solution has been devised by Mulder. It consists of a pear-shaped vessel, filled with the liquid, and fixed in a vertical position. It is provided with two glass taps for regulating the flow, and 20 drops are exactly equal to 1 c.c.

The agitator shown in Fig. 14 is a convenient appliance for shaking ten bottles at a time, and much saving of labour will attend the use of it where a considerable number of assays is frequently made. It consists of a metal frame, *m*, divided into compartments, *b*, *b*, *b*, to receive the bottles, and a lid, provided with spring slides, prevents the bottles from being displaced and the stoppers from being shaken out. The frame hangs from a short carriage spring, *s*, firmly fixed to the wall, by a leather strap or by india-rubber door springs, and it is connected with the floor by a long india-rubber spring, *p*.

Fig. 14.



A dead black shelf should be fixed in front of a window (which may be glazed with yellow glass) to receive the bottles during the addition of the decimal solution; and the shelf is provided with a black back of such a height that the light just passes through the upper part of the liquid contained in the bottles.

Additional Details with reference to the above Method.—If a small quantity of mercury be present in the metal under examination, it will, unless its prejudicial effect be neutralized, render the result of the assay inaccurate. Its presence may be at once detected by—(1) The permanence of the white colour of the chloride of silver, even when exposed to a strong light; and (2) The difficulty experienced in rendering the supernatant liquid clear by shaking. As already explained, the pure chloride rapidly becomes blue on exposure to chemically active light, and this is the reason for the employment of yellow glass or blinds to the windows by some assayers, as mentioned above. Should mercury be suspected, and the discoloration still take place, the question may be set at rest by taking 1 gram. or more of the metal, and only adding sufficient salt solution to precipitate, say, a quarter of the metal. The mercury will be first thrown down, and its effect will thus be concentrated on a small quantity of chloride of silver.

A convenient method of neutralizing the effect of mercury, even if only found to be present in the course of an assay, consists in adding acetate of soda or caustic ammonia and acetic acid, when, according to Debray, the nitrates of silver and mercury are transformed into acetates, an alkaline nitrate being

also formed. This authority, however, prefers to remove the mercury by previous fusion, in consequence of the difficulty in "clearing" which is occasioned by the use of acetates.

Mulder has shown that when the most exact chemical proportions of silver and salt react on each other, the addition of a solution of either will produce a precipitate—a fact which he considers due to the presence of nitrate of soda, but this explanation is doubted by Stas. Mulder points out, therefore, that an assay may be completed in either of the three following ways:—(1) By adding decimal salt solution until it just ceases to produce a cloudiness; (2) By adding a slight excess of salt, and then decimal silver until no more precipitate occurs; or (3) By finding the "neutral" point—that is, the point at which either the decimal salt or silver solution will produce the same amount of precipitate. He considers the last of these the most accurate, but the first is preferable from its rapidity; and if check assays be made from time to time, very great accuracy can be attained by its means.

It may be well to mention that as a rise of temperature occasions an expansion of the solution, it will render the "normal" liquid weaker, and therefore will tend to make the results appear too *high;* and a fall of temperature will have the reverse effect. It is very essential that the solutions be kept in well-closed vessels (of glass or earthenware), to avoid evaporation; and the exact strength of the normal solution should be ascertained each morning by one or two assays on fine silver. If it is found necessary to add salt solution, in order to reach the point at which no cloudiness is produced, it indicates that the solution is *weak;* the results therefore appear too *high*, and the excess must be deducted. When it is necessary to add silver solution, the reverse is the case; and the solution being too strong, the results appear *low*. Therefore it is necessary to add to all the results the amount represented by the additional silver solution introduced.

Pisani's Method.—This, which is specially applicable when only small quantities are present, cannot be used in presence of bodies which exert a decomposing action on iodide of starch—such as salts of mercury, and many of those of tin, antimony, arsenic, iron, manganese, and gold, or of substances which colour the solution. The process depends upon the fact that if solutions of iodide of potassium and starch be gradually added to a liquid containing nitrate of silver, no permanent blue colour is produced until all this salt is decomposed. Pisani's method, as modified by Vogel, is very convenient for photographers. The following solutions are required:—10 grams. of commercially pure iodide of potassium are dissolved in distilled water, and diluted to a volume of 1023·4 c.c.; 1 c.c. of this solution will suffice to precipitate 0·01 gram. of silver. One gram. of pure sulphate of monoxide of iron is added to 1000 grams. of nitric acid, of specific gravity 1·200, in order to obtain free nitrous acid; a small quantity of the iron salt must be added from time to time. The starch solution is made by dissolving 1 part of starch in 100 of warm water. This is allowed to settle; and after the clear liquid has been decanted, 20 parts of pure nitrate of potash are added. It will remain fit for use for about six weeks.

The following is the method of procedure:—1 c.c. of the nitric acid is added to 1 c.c. of the solution under examination, then 10 or 12 drops of starch solution and a few drops of the iodide, and the whole shaken. The addition of the latter is continued until a permanent pale blue coloration is just produced, and the number of c.c.s added indicates, without calculation, the number of centigrammes present per centimètre of the solution—that is, grammes per litre.

Volhard's method is applicable even when a considerable quantity of copper is present. If a solution of sulphocyanate of potassium or ammonium be added to an acid solution of a silver salt containing a small quantity of ferric sulphate, the whole of the silver is precipitated; and the least excess of the precipitant causes a blood-red coloration, owing to its combination with the iron salt. Hence if a standard solution of sulphocyanate be used, it will at once indicate the amount of silver present. As the sulphocyanate of ammonium is exceedingly hygroscopic, a standard solution must be prepared as follows:—10 c.c. of a solution of nitrate of silver, containing 10·8 grams. of pure silver per 1000 c.c., are introduced into a beaker, together with 5 c.c. of a solution of ferric sulphate (50 grams. per litre of water), and a solution containing about 8 grams. of the ammonium salt added gradually until a permanent pale red tint is obtained. A hundred times the amount so added is diluted to 1 litre, and each c.c. of the resulting solution is equivalent to 10 milligrammes of silver.

Preliminary Volumetric Assay.—As already mentioned, it is essential that the composition be approximately known, in order to successfully practise the wet method of Gay-Lussac. This may conveniently be determined by dissolving 1 gram. of the alloy in nitric acid, and very carefully precipitating with the normal salt solution. Thus suppose 70 c.c.s are required for this purpose, we have, $100 : 1{\cdot}0 :: 70 : x$, or $x = 0{\cdot}7$; and, to ascertain the amount of alloy to be taken for the assay proper, $0{\cdot}7 : 1 :: 1 : x'$, whence $x' = 1{\cdot}428$ gram.

Blowpipe Assay.—This account of the methods of assaying silver would not be complete without some description of the method of determining the amount of the precious metal in either ores or alloys by means of the blowpipe, which was first proposed in 1827 by Harkort, and considerably improved by Plattner. A very complete account of the method will be found in the *Chemical News* for 1867, by David Forbes, who practised it with great success. It is exactly analogous to the furnace assay before described, the fusion with lead, scorification, and subsequent cupellation being performed in all cases before the blowpipe. In the cupellation, however, the process is somewhat modified.

If the silver be already alloyed with lead, and be

free from such metals as would interfere with its treatment on the cupel, it may be at once submitted to cupellation; but otherwise, it must be scorified on charcoal until these substances are removed by volatilization or by slagging off. The concentration of the silver, as well as the final cupellation, take place on specially formed cupels 0·7 inch in diameter and 0·4 inch high, made of moderately fine bone-ash, which is, for the cupellation process, covered with a layer of bone-ash of very fine quality. The silver-lead alloy is submitted to the action of an oxidising flame, and quickly assumes a bright metallic appearance, commencing at the same time a rapid rotatory movement. This operation should be conducted at as low a temperature as is compatible with such a movement, otherwise the litharge is liable to sink into the cupel. The concentration must not be carried too far, as the silver would then be liable to spit. The cupel is now withdrawn very gradually from the flame and allowed to cool, when the metallic globule is removed from the litharge surrounding it.

In cupelling this button, it is placed in the centre of the cupel, and an oxidising blowpipe flame is made to play on the bone-ash surface immediately surrounding it without touching it, so as to insure the absorption of the litharge by the cupel, and to prevent scales of litharge being formed beneath the globule itself.

Considerable practice is required in order to properly conduct the process. It is, however, well worthy of more attention than it has hitherto received, and is capable, in able hands, of giving very excellent results.

STATISTICS.—The more important statistics relating to silver have been already given in the article on GOLD; but it may be interesting to add the accompanying table, which shows the produce of different parts of the world in 1800, 1850, and 1865:—

TABLE SHOWING THE APPROXIMATE YIELD OF THE PRINCIPAL SILVER-PRODUCING COUNTRIES OF THE WORLD (PHILLIPS).

COUNTRY.	1800.		1850.		1865.	
	Pounds Troy.	Percentage of Total.	Pounds Troy.	Percentage of Total.	Pounds Troy.	Percentage of Total.
Russian Empire,	58,150	2·5	60,000	2·1	58,000	1·5
Scandinavia,	141,000	6·0	20,400	0·7	15,000	0·4
Great Britain,			48,500	1·7	60,500	1·5
Hartz,			31,500	1·1	28,000	0·6
Prussia,			21,200	0·7	68,000	1·7
Saxony,			63,600	2·2	80,000	2·0
Other German States,			2,500	0·1	2,500	—
Austria,			87,000	3·1	92,000	2·2
France,			5,000	0·2	18,000	0·4
Italy and Sardinia,			—	—	25,000	0·6
Spain,			125,000	4·4	110,000	2·8
Australia, New Zealand, British Columbia, and Nova Scotia,	—	—	10,000	0·4	9,500	0·2
Chili,	18,300	0·8	238,500	8·4	299,000	7·3
Bolivia,	271,300	11·6	130,000	4·6	136,000	3·3
Peru,	401,850	17·2	303,150	10·7	299,000	7·4
New Granada,	5,000	0·2	13,000	0·5	15,000	0·4
Brazil,	1,200	—	675	—	1,500	—
Mexico,	1,440,500	61·7	1,650,000	58·4	1,700,000	42·3
United States,	—	—	17,400	0·7	1,000,000	25·0
Total,	2,337,300	100·0	2,827,425	100·0	4,017,000	100·0

SOAP. — *Savon*, French; *Seife*, German; *Sapo*, Latin.—The term soap was formerly applied to all compounds consisting of an alkali, an alkaline earth, or a metallic oxide, united to a fatty or oily acid, or other substance of an unctuous or oleaginous nature. This extended meaning of the term is, however, not now recognized; it is now applied to those combinations of grease or oil with the alkalies which, by their peculiar properties and solubility in water, aid the removal of grease and dirt in the processes of washing and scouring. This cleansing influence is due to what is termed a detergency; that is, a power of rendering soluble in water the adhering dirt of the clothes and the skin, to which purpose soap is almost exclusively applied. The alkalies themselves —potash and soda—possess this property of detersiveness; and the former, potash, under the form of wood ashes, was used in the most ancient times by the Hebrews, Egyptians, and Greeks, as an aid to cleansing processes. Free alkali itself, however, possesses a solutive property over fibrous materials, over even human skin, and hence the necessity of combining it in such a manner as to modify this injuriously corrosive action.

The remedy is the substitution of soap, which, by its slight excess of alkali, rendering soluble in and miscible with water all the dirty grease of the clothes and oily exudations from the pores of the skin, is at the same time detersive itself; for though composed of oil and alkali in a state of combination, it still possesses the influence of the latter without any of its hurtfulness. Oleate of oxide of lead, formerly called *lead soap*, is insoluble, and constitutes the diachylon plaster of pharmacy. The analogous salts of zinc and lime, formerly termed *zinc soap* and *lime soap*, are also insoluble.

Historical Notice.—Although the word *soap*, or rather *sope*, is occasionally met with in the translation of the sacred records, it must not be supposed that the substance now known by that name was used by the Israelites. The word so rendered doubtless refers to the juice of some plant, or more probably to the ashes of a plant; as the substance in question appears to have detersive properties. The earliest mention of the term *soap*, as applied to the substance now under discussion, occurs in the writings of Pliny, who also describes a process for its preparation differing but little from that pursued at the present day. This writer ascribes its invention to the Greeks, from whom the Romans, and subsequently other nations, derived a knowledge of its manufacture. Homer makes no mention of soap, and it was doubtless unknown to him. In the excavations at Pompeii a complete soap-boiling establishment was discovered, containing soap still perfect, though it must have been prepared upwards of seventeen hundred years.

The Germans were at a very early period distinguished for their production of superior soap, and hence probably the Latin term *sapo*, from the original German *seipe*, now written *seife*, and from this by a transposition of letters the English *soap* is derived. Owing in a great measure to natural advantages of the country, France is now a great mart for soap, and especially for toilet soaps.

Materials.—The materials used in the manufacture of soap are various kinds of oil or fat, resin, and the alkalies, potash and soda. All oils and fats of whatever kind, vegetable or animal, yield soaps when treated with alkali. Only a very limited number, however, is used in this manufacture. In Great Britain palm oil is consumed in greater quantity than any other, and principally in the production of hard soap; for soft soaps, the various kinds of fish oils, the drying oils from seeds, and tallow are mostly employed.

In France, and on the Continent, olive oil is extensively used in soap-making; for soft soaps hemp-seed oil.

Tallow, saponified with soda, yields white curd soap; this is superseded in great part by the softer and otherwise superior palm-oil soap. Cocoa-nut oil soap, on account of its property of dissolving pretty readily in salt water, is useful for washing during long sea voyages. Of all soaps the most emollient are those of palm oil, castor oil, and of spermaceti.

Most of the oils and fats are met with in commerce in a sufficient state of purity for their conversion into soaps without previous preparation.

Palm oil, however, and occasionally tallow, are exceptions to this rule, and therefore the methods most effectual for their purification before being used in the manufacture will be afterwards stated.

The mixture of oleic acid with small quantities of stearic and margaric acids, which is obtained in the separation of stearic acid by pressure, affords an excellent soap.

Experiments were made by Darcet, Lelièvre, and Pelletier, on the relative value of different kinds of oil and fat in the manufacture of soap. The oils or fats were saponified by means of caustic soda lyes, and the products were, therefore, soda soaps. The results of these experiments were as follows:—

Olive-oil soap.—3 lbs. of olive oil gave a block of soap weighing 6 lbs. 10 ozs., which on exposure to the air for two months became 4 lbs. 15 ozs. It was then dry and perfectly solid, of excellent colour, resembling that of Marseilles soap. By further exposure in a dry place it became still lighter, owing to loss of water.

Sweet almond-oil soap was found to be next to the olive-oil soap in consistency. This was very white, uniform, and of an agreeable odour. Its weight from 3 lbs. of oil was 5½ lbs.; and after two month's exposure it lost 1 lb. of water.

Rape-seed oil soap is of a greyish-yellow hue, is more consistent than that of colza oil, and possesses the peculiar odour of the oil from which it is produced.

Oil of beech-nut soap is of a dirty-grey colour, softer than the preceding, and has the smell of the oil. This soap is greasy, pasty, and clammy, and when exposed to the air becomes yellow.

By associating these oils with proportionate quantities of suet or tallow, mixtures will be formed, of which soaps of proper quality and consistence can be made.

Poppy oil.—The soaps made from this oil are of a dirty grey, without any disagreeable smell; are clammy, and of medium consistence. They become yellow in the air, and when exposed to cold become soft at the surface. This oil, when mixed with the greases, yields a soap much resembling in appearance that of olive oil.

Hemp-seed oil soap is of a green colour, very pasty, and so soft that the least addition of water renders it liquid. Exposed to the air, it loses its green tint exteriorly, bleaches, and afterwards becomes brown. *Nut-oil soap* is of a yellowish-white colour, with but little consistence, is greasy and clammy, and assumes a brown appearance on exposure. *Linseed oil* yields a whitish soap, which, however, becomes yellow by contact with the air. This soap is greasy, pasty, and viscous, of a slight consistence and powerful odour, and is reduced to a thin paste by a slight addition of water. *Sperm-oil soap* is of a dirty-grey colour. It retains the peculiar smell of the oil, becomes reddish-brown and of some firmness, but much less than olive-oil soap.

Fish oil is very similar to the last named.

Cod-liver oil soap differs only in having a more unpleasant smell and less consistency.

Suet or tallow soap is white and solid, and has a slight odour of the fat. Exposed to the air, it loses water and becomes brittle. Soap prepared from *lard* is very white, solid, inodorous, and especially valuable for the production of toilet soaps.

Rancid butter yields a soap which is white, and in properties similar to tallow soap, but retains a rancid smell.

Castor-oil and *spermaceti* soaps are emollient, and especially applicable to toilet purposes.

Palm-oil soap is little inferior to castor-oil or spermaceti soap. When combined with rosin, it constitutes the well-known "yellow soap."

Lastly, soaps prepared from drying oils are usually soft and flabby.

The appended table shows the quantity of soap obtained from 3 lbs. of each of the oils mentioned above, saponified with caustic soda solution.

Oil or Fat.	Colour of the Soaps.	Quantity obtained as taken from the frame.	Loss of Weight in Lbs. and Ozs.	Time.
Olive oil,	White,	6 lbs. 10 ozs.	5 lbs. 0 oz.	2 months.
Sweet almond oil,	White,	5 " 11 "	4 " 6 "	2 months.
Colza oil,	Lemon-yellow,	5 " 14 "	5 " 0 "	15 days.
Rape-seed oil,	White,	6 " 8 "	5 " 0 "	20 days.
Beech-nut oil,	Dirty-grey,	5 " 4 "	4 " 13 "	2 months.
Poppy oil,	Grey,	4 " 8 "	4 " 6 "	45 days.
Hemp-seed oil,	Green,	5 " 0 "	4 " 14 "	15 days.
Nut oil,	Deep yellow,	4 " 7 "	4 " 6 "	15 days.
Linseed oil,	Yellowish	5 " 0 "	4 " 12 "	1 month.
Sperm oil,	Dirty-grey,	4 " 12 "	4 " 10 "	15 days.
Fish oil,	Reddish-brown,	4 " 11 "	4 " 8 "	1 month.
Cod-liver oil,	Dirty grey,	4 " 14 "	4 " 12 "	15 days.
Suet or tallow,	White,	8 " 4 "	6 " 0 "	2 months.
Lard,	White,	8 " 3 "	5 " 0 "	2 months.
Washed rancid butter,	White,	11 " 0 "	7 " 0 "	2 months.

Palm Oil.—As it arrives in this country, this oil is tinged with a peculiar and characteristic orange-red colour, which renders it unfit for use for soap making in its natural state. This colouring matter is not proper to the pure oil, which in a state of chemical purity is perfectly colourless. There is associated with the oil, however, and extracted with it from the palm, a peculiar principle which in the course of time undergoes spontaneous decomposition, assuming at the same time a characteristic colour.

Numerous processes have from time to time been adopted to effect the decoloration of palm oil, nearly all of which depend upon the application of nascent oxygen produced through the decomposition of various compounds, from which it may be liberated with a greater or less degree of facility.

The old method consisted in the employment of nitric acid, but this method has the disadvantage of impairing the peculiar violet odour of the oil upon which its value chiefly depends; whilst, at the same time, though the colouring matter is destroyed, the oil is not perfectly bleached, and hence it yields a soap of a greyish-yellow hue. Neither is chlorine well adapted for the purpose, though the colouring matter is readily decomposed by it; for this agent exerts an injurious action on the oil itself, developing a brown tint, and impairing its consistence.

Of all methods of bleaching palm oil, the best is that originally proposed and patented by Watt, in which the decoloring agent is nascent oxygen produced by the decomposition of chromic acid. The process is commenced by heating the oil by steam in an ordinary boiling cauldron for half an hour; it is then allowed to stand at rest to deposit impurities, and when cooled down to about 130° Fahr., it is drawn off from the sediment and condensed steam, and placed in wooden vessels, each capable of containing 2 or 3 tuns. To each half tun of oil, thus freed from extraneous matters, the following mixture is added:—A saturated aqueous solution of 12½ lbs. of bichromate of potash, 4 lbs. of concentrated sulphuric acid, and about 25 lbs. of strong hydrochloric acid. These proportions are not always strictly adhered to; many bleachers using to the above quantity of oil 10 lbs. of the bichromate, and 40 of the hydrochloric acid. After being well agitated with the mixture for a few minutes, the oil becomes of a black colour; in a short time, however, this changes to dark green, and soon afterwards to light green; and at the same time a thick froth appears on the surface, indicating the termination of the reaction. The oil is now examined by taking out a small portion and allowing it to settle, and if not sufficiently bleached an additional portion of the bleaching mixture is added.

After complete decoloration, which is effected in from ten to fifteen minutes, the oil is permitted to remain undisturbed for about half an hour, so as to allow the deposition of the aqueous solution of chloride of chromium, sulphate of potash, and other foreign matters, after which the clear oil is drawn off into a wooden vat, mixed with a little fresh water, and again heated for a short time by means of steam. After being once more allowed to rest to deposit water, &c., the oil is fit for use.

As already mentioned, the decoloration is effected in this process by the agency of nascent oxygen. When the solution of bichromate of potash and hydrochloric acid are mixed, the acid of the bichromate is liberated, the oxygen of the potash seizes the hydrogen of the acid, forming water, and the chlorine unites with the potassium to produce chloride of potassium, as represented in the annexed equation:—

Bichromate of Potash.		Hydrochloric Acid.		Chloride of Potassium.		Water.		Chromic Acid.
$K_2CrO_4.CrO_3$	+	$2HCl$	=	$2KCl$	+	H_2O	+	$2CrO_3$.

After this decomposition, the mixture, containing an excess of hydrochloric acid, is added to the melted oil; and on coming in contact with the organic matter, a further change takes place between the hydrochloric and chromic acids. The latter is reduced to chromic oxide, Cr_2O_3, and this with

hydrochloric acid yields chromic chloride, Cr_2Cl_6; water is formed, and oxygen is set free as follows:—

Chromic Acid.		Hydrochloric Acid.		Sesquichloride of Chromium.		Water.		Oxygen.
$2CrO_3$	+	$6HCl$	=	Cr_2Cl_6	+	$3H_2O$	+	$3O$.

The liberated oxygen is seized by the colouring matter, and the green sesquichloride of chromium, chloride of potassium, &c., are found in solution in water at the bottom of the vat. The sulphuric acid directed to be added by the inventor does not appear to be essential to the operation, and is indeed omitted by many bleachers. Oil once bleached by this process may be preserved from acquiring colour, and the soap made from it does not become tinged like that made from oil bleached by other methods.

When palm oil is to be used in the production of yellow soap, the most economical mode of bleaching is by the process invented by Arthur Dunn. This method, which is also applicable to other oils and fatty matters of a like nature, consists in the exposure of the oil to the combined influence of air and heat. The air is forced beneath the surface of the oil through pipes, by means of a blowing apparatus, and then allowed to rise through the liquid in numerous small streams—the oil being maintained at a temperature between 170° and 230° Fahr. by steam pipes or other means. A hood communicating with a chimney is placed over the vessel containing the oil, for the purpose of conducting away the unpleasant vapours which are disengaged.

According to Parnell, the oil should not be maintained at a temperature exceeding 180° Fahr. during the operation of blowing in the air. He recommends, however, that at the commencement of the process it be heated to 212° Fahr., and then suffered to cool a little. This is necessary, inasmuch as the air has but little effect as long as water is present; but when this is completely expelled, the bleaching commences immediately.

The oxidising action of the air on the colouring matter of palm oil seems to be accelerated by combining the influence of light with that of heat. With this end in view, the oil is sometimes placed in a thin layer on the surface of a large shallow uncovered vat. Several of these vats, each about a foot in depth, may be heated by means of steam passed through serpentine leaden pipes proceeding from a common boiler; one extremity of each tube may terminate in a receiver for the condensed water, and the latter may be returned to the boiler. Each vat is first two-thirds filled with water; and when this is hot, a sufficient quantity of palm oil is introduced to form when fluid a layer of about 2 inches in depth, and this should be maintained during the whole process at a temperature as near 212° Fahr. as possible. To preserve an equal temperature throughout the fluid, the steam may be admitted at opposite ends of the vat, and separated in contrary directions by two distinct serpentine tubes. Both air and light having access, the time required for the decoloration of the oil is from ten to fifteen hours—the thinner the stratum of oil, the more rapid is the process. The rapidity of the bleaching action is not sensibly lessened by loosely covering the containing vessel, provided the removal of the air over the surface of the oil is not much interfered with; but if exposed to a temperature of 212° in a closed vessel, so that although light and heat have access the air is excluded, the oil does not then become bleached. The bleached oil, which while fluid retains a fawn-coloured tint, is after solidification of a greyish-white colour.

Rosin.—Besides oil and alkali, common rosin or colophony also forms an important ingredient in the production of soap. The kind used is that yielded by the common turpentine, produced by and extracted from the several species of pine.

Though employed in the fabrication of soap as a partial substitute for oleaginous or fatty material, rosin does not possess a similar constitution to these matters, and therefore does not suffer an analogous alteration in the process of saponification. The introduction of too large a proportion of rosin into soaps gives them a very dark colour, and also renders them much too soft. Rosin is only used in the production of yellow soap. A process for bleaching rosin has been patented by Messrs. Hunt & Pochin of Manchester. They melt the rosin and then pass steam through it.

Alkalies.—The alkaline ingredients employed in the soap manufacture are potash and soda. Both these articles are met with abundantly in commerce in the state of carbonate, and in this condition purchased by the soap manufacturers.

The sodium carbonate now used by soap manufacturers is bought as white ash or soda ash.

This ash contains carbonate of soda sometimes to the amount of 95 or 96 per cent. It is essentially necessary in the production of soap that the alkali should be rendered caustic—that is, set free from carbonic acid; as, if combined with even the weakest mineral acids, these will not be displaced by the fatty acids, and saponification will not ensue. The greatest care should therefore be exercised in this preliminary process—the preparation of the lyes. The process for causticizing is the same in principle for the preparation both of soda and potash lyes. It depends upon the greater affinity of calcium than of sodium or potassium for carbonic acid, and the decomposition is one of the most simple, thus—

Sodium Carbonate.		Calcium Hydroxide.		Calcium Carbonate.		Sodium Hydroxide (Caustic Soda.)
Na_2CO_3	+	CaH_2O_2	=	$CaCO_3$	+	$2NaHO$

The proportions of soda ash and lime employed vary according to the degree of strength of the soda; similarly with regard to the potash salt. It is, however, always an advantage to have an excess of lime over the alkaline carbonate, as in the contrary case any undecomposed carbonate is totally lost.

In England the lyes are made by boiling together the soda ash and lime: on the Continent the ingredients are mixed in the cold. The proportions are 50 lbs. of lime to 100 lbs. of carbonate of soda, 80 lbs. of lime to 100 lbs. of carbonate of potash.

The soda ash or potash and lime (slaked with hot water) are thrown into a vat and boiled by a jet of steam for several hours, until the supernatant liquor

no longer gives off carbonic acid on being treated with hydrochloric acid. The lye thus made contains less lime than that made in the cold. When the calcium carbonate has entirely subsided the liquor is drawn off into tanks. The residual precipitate is washed with water, and the weak liquor is used for diluting stronger lyes, or in place of water for the next causticizing operation.

A fact deserving of mention in treating of the preparation of lyes is, that in the process of causticizing by means of lime, a portion of the soda appears to enter into some form of combination very difficultly soluble. Kynaston found the residue to contain, after being well washed, soda to the amount of 5 or 6 per cent. When the deposit, after being dried, is heated to a temperature insufficient to expel carbonic acid, and after being allowed to cool is again drenched with water, caustic soda is then removed with great ease, and the deposit may be almost completely deprived of soda. Taking these facts into consideration, it is very probable that it would well repay the soap manufacturer to collect the lime deposit, and after thorough desiccation by exposure to the air, to submit it to heat until the carbonic acid is expelled. The lime now again become caustic may be used advantageously in the preparation of fresh lye, and the process may be repeated until the deposit becomes highly charged with the impurities of the ash, when fresh lime may again be used for a new process.

The addition of alum to soda lyes is stated by Kottula to facilitate saponification. The lyes are made hot, and the alum added in the following proportions:—

Alum.	1 cwt. lye.
12 ozs.	10° B.
18 ozs.	15° B.
24 ozs.	20° B.
30 ozs.	25° B.

Another of those progressive steps manufacturers frequently take, leading to the simplification of operations which previously had been tedious, laborious, and wasteful, has been taken in the soda trade, the especial benefits of which are to be derived particularly by the soap-maker and the public generally. This intellectual advancement consists in preparing *directly* the caustic alkali, by the use of which the soap-maker at once dispenses with a considerable plant outlay, economizes space, expedites the operations of his trade, and effects no little amount of saving in labour alone, compared with the present general practice. Besides the foregoing immediate and apparent advantages resulting in favour of the soap-maker from the employment of caustic soda prepared *directly*, there are others of much greater importance—namely, the economy of alkali, and the readiness with which soap can be made by the use of lyes, the strengths of which are immediately under control, and which cannot be obtained economically on the present causticizing system to which soda ash is submitted, unless at considerable trouble; and even then the lyes are not pure, owing to the circumstance that strong caustic alkaline solutions divest carbonate of lime of a portion of its carbonic acid.

Of late years caustic soda for soap-making has been manufactured to a very considerable extent by alkali-makers, and the trade is likely to be greatly increased; and it is evident that its employment would be much more economical to the soap manufacturers than the present method of preparation. The caustic soda requires simply to be dissolved in a given quantity of water to produce lyes ready for use and of any required strength.

Testing the Lye.—For this purpose specific gravity bulbs, or the *hydrometer*, is used. In this country Twaddell's hydrometer is most commonly employed. The degree indicated by Twaddell's hydrometer, multiplied by 5 and added to 1000, expresses the specific gravity of the fluid. A lye testing 27·50 Twaddell, for instance, has a density equal to 1·138, which is equivalent to 15 per cent. of potash or 12·8 per cent. of soda, always supposing the lye to contain no other matters or salts which might also affect the specific gravity. This, however, is never the case with soap-boilers' lye, so that the indications are only approximations with reference to the amount of alkali, or even may be altogether fallacious. Still they are useful in a variety of ways, and are indeed indispensable. The practitioner is able with this instrument to follow the diminishing strength of the liquid flowing from the ash tubs or vats, and to form a just estimate of its value, when, at the same time, a test with acid proves the absence of carbonic acid. But even in the process of soap-boiling itself, the test of the lye afforded by the hydrometer, combined with the personal experience of the workman, is a clue by which he is enabled to judge whether the proper strength has been attained; knowing as he does what degree the hydrometer ought to indicate from any particular soda or potash lye for any particular purpose. The more or less caustic taste of a lye is also a test much depended on by many soap-boilers.

Saponification.—Oils and fats themselves are neither soluble in water nor miscible with it, but nearly all are made so by union with alkali. The process of effecting this combination is termed *saponification*, and the compound produced is *soap*—hard soap when its base is soda, but a more or less soft soap when potash is the alkali present.

The properties and composition of oils and fats have already been described. It is sufficient to state here that neutral fats, such as tallow, palm oil, cocoa-nut oil, &c., are the glyceryl salts of the fat acids; and their conversion into soap or "saponification" consists in the separation of the glyceryl and the acid, and results in the formation of an alkaline salt of the fat acid (*i.e.*, a soap) and glycerin, thus—

$$\underset{\text{Stearine.}}{\left.\begin{matrix}(C_{18}H_{35}O)_3\\(C_3H_5)\end{matrix}\right\}O_3} + \underset{\text{Potassium Hydrate, 3 Atoms.}}{\left.\begin{matrix}K_3\\H_3\end{matrix}\right\}O_3} = \underset{\text{Glycerin.}}{\left.\begin{matrix}(C_3H_5)\\H_3\end{matrix}\right\}O_3} + \underset{\text{Potassium Stearate, 3 Atoms.}}{\left.\begin{matrix}(C_{18}H_{35}O)_3\\K_3\end{matrix}\right\}O_3}.$$

In all saponifiable fats the same reaction ensues, though the soap produced contains different acids, according to the kind of grease or fat employed. Thus, in the case of palm oil, the soap consists for the most part of *palmitate* of sodium or potassium. When spermaceti is used, the soap produced consists of *cetylate* of potassium or sodium; and instead of glycerin, an analogous body termed ethal is found in the mother liquor. By far the greater majority of fats, however, yield when treated with alkalies soaps containing only stearate, palmitate, and oleate of potassium, if a soft soap, and of sodium in the case of hard soaps. Rosin, though employed in the manufacture of soap in the place of fixed oil or fat, is not to be considered analogous to a fat in its chemical constitution, or to be capable of forming with an alkali a proper soap by itself. Rosin is an indefinite mixture of three distinct bodies possessing well-marked acid properties; and hence named *sylvic*, *pinic*, and *colophonic* acids, each of which is capable of entering into combination with alkalies, and of readily dissolving in alkaline solutions, though totally insoluble in pure water.

For the complete saponification of fats or oils an excess of alkali is requisite; this is the more willingly employed, that it can be removed again without difficulty.

The production of soap is by no means a momentary process. On the contrary, the manufacture consists of a number of stages, and these occupy a considerable length of time from the first mixing of the fat with the alkali, when an emulsion is produced, to the formation of soap ready for use, or even to that point when the whole of the alkali is saturated with fatty acid. Acid salts are first produced with the oily acids, and these hold the remainder of the fat in solution, or in a state of division, until it also is able to combine with alkali, and transform the acid into neutral salts or into finished soap. This reaction may easily be observed, if the fat is boiled with one-half the required quantity of alkali; the whole of the oil is in such case dissolved, but the solution becomes turbid on cooling, and when water is added, and the mixture again boiled, unsaponified fat separates, showing that this had only been retained in the fluid by the stearate or margarate of the alkali that had been formed.

Hard and Soft Soap.—Soaps are divided into two classes, differing from each other in the material from which they are produced, and are distinguished by the names *hard* and *soft soap*. Hard soaps are made from fats, or vegetable fat oils, and soda; for soft soaps, the oleaginous material is usually a fish oil or vegetable drying oil, and the alkali, potash. Hard soaps may, however, be made with potash, provided a solid fat be employed; but soda soaps are invariably harder than potash soaps, the unctuous material being the same. The hard soaps of animal fats are either white or marbled, and are particularly applicable for washing the finer articles of dress, the soft soaps being more caustic than the solid soda soaps. Of the hard soaps of commerce those made with oils, with the exception of palm oil, consist of oleate, with only a small proportion of stearate of sodium; those made with animal fats are mixtures of stearate, palmitate, and oleate of sodium. On the Continent, and wherever wood is abundant, potash is frequently introduced in admixture with soda in the production of hard soaps.

Properties of Soaps.—Potash and soda soaps are readily soluble in hot water and alcohol; both solutions solidify to a jelly if concentrated. *Opodeldoc* is this jellied soap mixed with alcohol. The addition of a quantity of cold water to the aqueous solution produces a precipitation, the neutral salts of stearic and palmitic acids decomposing into free alkali, which remains in solution, and acid stearate and palmitate of alkali, which precipitates in the form of pearly, crystalline scales. Potash soaps are more soluble in water than those containing soda. Stearate of sodium may be regarded as the type of hard soaps; in contact with ten times as much water, it suffers no striking change, while stearate of potassium under the same circumstances forms a thick paste or a viscid solution. In these respects the palmitates of potassium and sodium closely resemble the corresponding stearates. Oleate of sodium is soluble in 10 parts of water, and oleate of potassium in 4 parts. The latter forms a jelly with 2 parts, and possesses such a strong affinity for water, that 100 parts absorb 162 when exposed to a humid atmosphere. It follows, therefore, that soaps are soft in proportion to the oleates, and hard in proportion to the stearates and palmitates they contain, so that the softness or hardness of soap is not solely dependent upon the base that is employed.

Soap of Commerce—that is, stearate, palmitate, or oleate of alkali—is never dissolved by cold water without decomposition. The neutral salts are resolved into alkali, which dissolves, and into an acid salt, which is precipitated. The same decomposition occurs when hot solutions of soap—particularly of dilute—are cooled.

The occurrence of these decompositions, which ensue equally with the palmitates and oleates of potassium and sodium, as with the stearates, affords an easy explanation of the appearance of the whitish turbidity always produced when soap is dissolved in even the purest water, and show, at the same time, that the alkalinity of soap-suds is solely due to the liberation of caustic potash or soda; and this it is that affords the possibility of removing fatty impurities in water, which is the sole object of washing with soap.

It is of the utmost importance to the soap-boiler that he be well acquainted with the physical comportment of soaps with solutions of different salts, as, for instance, with chloride of sodium, carbonate of soda, the corresponding potassium salts, chloride of ammonium, and various others. These, although not absolutely essential to the formation of soaps, are very much concerned in the separation of the foreign matters that render hard soap impure; and are also useful to impart to it the proper amount of water. In practice, a solution of chloride of sodium is always employed for this purpose. The peculiar

behaviour of soap with a solution of this salt was noticed by Liebig:—

If a piece of common hard soap be placed in a solution of salt at ordinary temperature, it floats upon the surface without ever being moistened, and if the liquid be heated to boiling, it separates without foam into gelatinous flocculæ, which collect on the surface, and upon cooling unite into a solid mass, from which the solution flows off like water from fat. If the flocculæ be taken out of the hot fluid, they congeal on cooling into an opaque mass, which may be pressed between the fingers into fine laminæ without adhering to them. If the solution is not quite saturated, the soap then takes up a certain quantity of water, and the flocculæ separate through the fluid on boiling. But even when the water contains only $\frac{1}{400}$th part of common salt, ebullition does not produce solution. If the soap is boiled in a dilute and alkaline solution of salt, and suffered to cool, it again collects on the surface of the fluid in a more or less solid state, depending on the greater or less degree of concentration of the solution; that is, on the quantity of water taken up by the soap. By boiling the dilute solution of salt with soap for a considerable time, the aqueous flocculæ intumesce, and the mixture assumes a foamy appearance, but still they are not dissolved, as the solution separates from them. The flocculæ, however, have become soft and pasty even after cooling, and their pastiness depends on the quantity of water they have imbibed. By still continued boiling this character again changes, and in proportion as the water evaporating renders the solution more concentrated, the latter again extracts the water from the flocculæ; the liquid, however, continues to foam, but the bubbles are larger. At length a point is attained at which the solution becomes saturated; the larger iridescent bubbles formed just before disappear, and the liquid continues to boil without froth; all the soap collects as a translucent mass on the surface, and now the solution and soap cease to attract water from each other.

If the plastic soap be now removed and cooled, while the solution is pressed out, it becomes so solid as scarcely to receive an impression from the fingers. In this state it is called *grain soap*. The addition of salt, or its solution, to a concentrated alkaline menstruum of soap in water, precipitates the soap in gelatinous flocculæ, and the mixture behaves precisely as solid soap boiled with a dilute solution of salt. Caustic potash and carbonate of potash act like salt in separating soap from the alkaline fluid. The application of these facts to the manufacture of soap is obvious. The fat is kept boiling in an alkaline lye until all pasty matters disappear; but the lye should have such a strength that the soap may be perfectly dissolved in it. Thus tallow may be boiled for days in a caustic potash solution, of specific gravity 1·25, without being saponified. If the lye be stronger a partial saponification ensues; but being insoluble in the fluid, the soap floats on the surface as a solid mass. By the gradual addition of water with continued boiling, the mass at a certain point becomes thick and clammy, and with more water an emulsion is formed; on continued heating this becomes perfectly clear and transparent, if a sufficient quantity of alkali be present. In this state it may be drawn out into long threads, which on cooling either remain transparent, or are milky and gelatinous. As long as the hot mass, suffered to drop from a spatula, exhibits a milkiness or opalescence, the boiling is continued, or more alkali added. When excess of alkali is present, the milkiness arises either from imperfect saponification or want of water; the former is known by dissolving a little in pure water, which becomes perfectly clear when the whole is saponified.

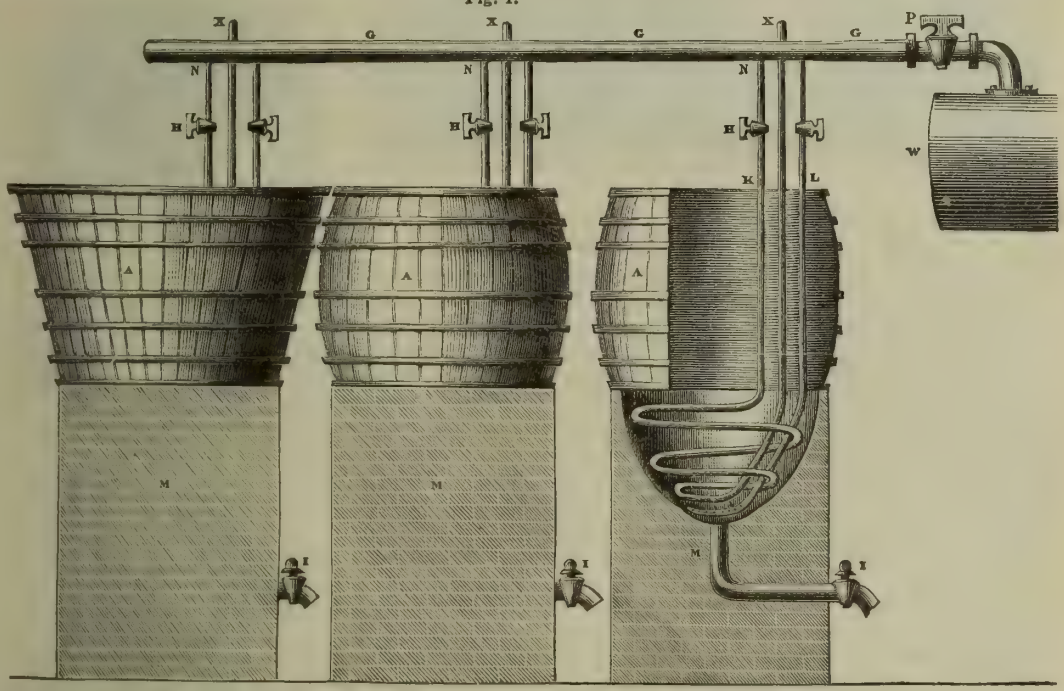
If the lye contains lime the mixture is also turbid, but the addition of an alkaline carbonate causes the turbidity arising from this cause to disappear instantly. In order to separate the soap from water, free alkali, and glycerin, a large quantity of salt is gradually added to the boiling mass, waiting after each addition till that portion is completely dissolved. The first addition increases the consistency of the mass, while each successive portion renders it more fluid, till it loses its adhesive character, and drops from the spatula in short thick lumps. As soon as the congelation is complete—that is, when gelatinous flocculæ separate from a clear watery liquid—the fire is extinguished, the soap allowed to collect on the surface, and cooled either on the liquid, or ladled out and allowed to get solid.

In being separated by means of salt from a very dilute solution, soap suffers an alteration in composition, the soap so thrown down being a distearate, dipalmitate, or dioleate of the alkali, instead of the neutral compound originally in solution; but when the solution is of moderate strength, the soap is separated unaltered in composition. The same results as those obtained by the use of common salt are also produced, although in a less energetic manner, by chloride of potassium, carbonates of the alkalies, sulphate of soda, acetate of potash, and chloride of ammonium. Of these, sulphate of soda and chloride of potassium have but a very slight action. Concentrated caustic lyes also separate soap from its solution, in the same manner as with common salt; in weak caustic lye, on the contrary, soap is perfectly soluble. On this account soap-boilers, especially at the commencement of the operation, except in the case of cocoa-nut oil, always use weak lyes, as the stronger would prevent the necessary amount of contact amongst the ingredients, and very much retard the process of saponification. Not only all foreign matters other than soaps, but also the base of the oils—glycerin—is completely separated from soap by means of caustic or saline solutions, in which it is perfectly soluble. The separation of the small quantities of earthy and metallic soaps, always formed during the process of saponification by means of impure alkalies, requires a distinct operation, termed the *fitting* process, which will be presently alluded to.

Manufacture.—The boilers used in the soap manufacture are formed of cast-iron or wrought-iron plate. Their capacity varies according to the quantity of soap to be produced—some being as large as 15 feet

in diameter and 15 feet deep, and capable of yielding 25 to 30 tons of soap at one operation. The pan or kettle is fixed in the brickwork, and so built round that the heat acts solely at the bottom. The waste lyes are withdrawn from the bottom by means of a pipe fixed to the boiler. The pans are usually cast with a flange at the upper rim, so that if necessary the boiler may be enlarged by adjusting a hollow cone of wood, iron bound, and which is termed the *curb*. It may extend as high as desired, and should be surrounded with mason work like the rest of the pan. The boiling of the soap is accomplished by means of steam, either conducted directly into the materials in the boiler, or when a high temperature is not desirable, by applying the steam to the outer surface of the caldron. The application of steam is a method of communicating heat to the caldrons far preferable to the old method of placing the boiler directly in contact with the fire. Not only is there a great saving of fuel, but less attention, and consequently fewer hands are required, while the facility of arresting the operation at any desired moment is of great importance. In the annexed representation (Fig. 1) are shown three caldrons, A, A, A, set in solid masonry, M. The main pipe or steam feeder, G, is attached by the cock, P, to the boiler, W, which is stationary, and generally placed against the wall immediately above the kettles or caldrons. These latter are partly of iron and partly of wood, the upper portion or *curb* being wood, well hooped round by iron rings, and the lower portion of cast iron, and so shaped that the worm can lie closely to the sides, and that the blow-pipe can fit upon the bottom. The steam is admitted

Fig. 1.



to the vats by the cock, H, on the pipe, N. In the section at K the position of the coil is displayed; the waste steam is led away at X. The cock, I, is for the withdrawal of the spent lyes. The pipe, L, serves when necessary to communicate additional heat to the contents of the pan, and is useful also to agitate the mass. In some manufactories the boiling vats are made wholly of wood, well fastened by iron clamps.

Another arrangement of soap caldrons is shown in Fig. 2. A is the steam boiler; B B, the soap pans; C, the chimney; D, the steam chest, whence the serpentine coils. S S, are supplied with steam by the pipes, E E. The lyes are withdrawn from the pans by the cocks, I I, and the condensed water from the coils by the cocks, H H.

The process is rendered more rapid and fuel is saved by employing superheated steam. An ingenious contrivance of Morfit's for this purpose is shown on next page.

This apparatus (Fig. 3) is used for mixing, stirring, and heating, at one and the same time, the contents of vessels of any size or form, by superheated steam. It is well adapted for the manufacture of soap. A is the containing vessel, which may be a pan with a round bottom or a wooden tub. Firmly fixed to the centre of the bottom of this vessel is a slightly conical metallic socket, communicating with a waste pipe, L; and adjusted to and turning in this socket is the upright metallic shaft, C, carrying the tubular arms or coils, D D, *e e*, arranged in horizontal and vertical series alternately. There may be two, four, or more of these series of branching tubes. Each is tightly joined with the shaft at F, the centre of which is hollow from that point upwards to the stuffing box, G, as a passage way for

the steam from the generator to the rotating arms. The lower end of the shaft is also hollow in the centre to a height of several inches above the bottom of the pan, for the purpose of communicating from the feed-pipe, K. down into the tubular arms of the twirl, which twirl being made to revolve simultaneously by power applied to the gearing, H J, the stirring and heating of the contents of the pan go on uninterruptedly together.

Fig. 2.

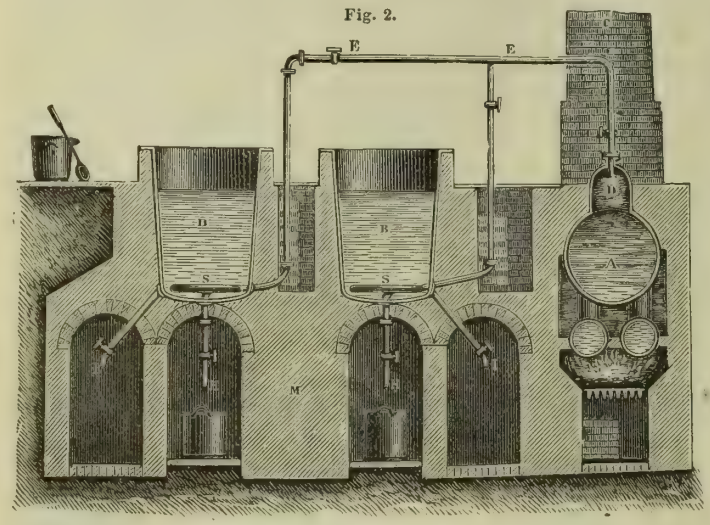
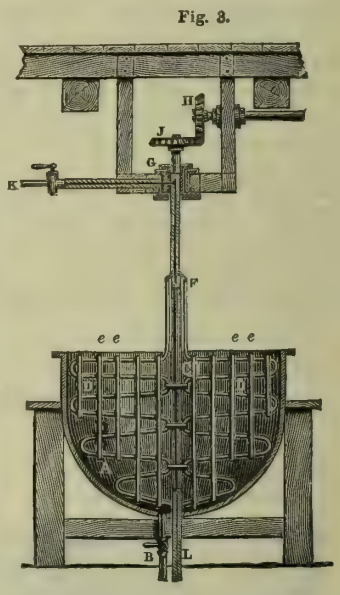


Fig. 3.



W. Gossage of Widnes thus describes the method of making English hard soaps:—The manufacturer provides himself with solutions of caustic soda of various strengths, called lyes, these being obtained by boiling together a solution of carbonate of soda and slaked lime, running off the first solutions and washing the residual carbonate of lime with several affusions of water; the last liquors thus obtained being used for dissolving a fresh batch of carbonate of soda.

It is a well known fact that lime, in whatever proportion it may be used, does not effect the perfect decomposition of carbonate of soda, unless the latter is present as a weak solution. And as any alkali in the state of carbonate which may be introduced into the soap-copper is incapable of decomposing the neutral oils or fats, it becomes wasted; therefore the manufacturer uses solutions of carbonate of soda of such strength as will yield lyes (solutions of caustic soda) having a specific gravity not exceeding 1·090.

The manufacturer charges his soap-pan at the commencement with a quantity of neutral fat or oil, and adds to this weak lyes having a specific gravity of about 1·050. He causes steam to be injected to produce ebullition and mixing. If the process goes on properly the oil or fat which was previously floating on the surface of the lye becomes speedily combined with it, producing a uniform milky emulsion, from which no watery particles separate on cooling. If this combination does not take place, the operator adds either water or weaker lye, and between the exit ends of the branches and the waste pipe, L.

The gearing by which the twirl is made to revolve is shown at H J. The superheated steam passes continues the boiling until a perfect emulsion is produced. At this period all taste of alkali in this compound has passed away—the tongue being used by the operator in place of turmeric paper to ascertain the presence of free alkali. The combination of the oil or fat with the mineral alkali, or the displacement of the glycerin, having been thus fairly put in progress, the operator makes repeated additions of stronger lyes, continuing the boiling until he finds the presence of free alkali in the compound; he then adds more oil or fat, or some rosin (if he is making soap containing rosin); he also continues to make repeated additions of stronger lyes. In this part of the operation he takes care there shall be no excess of alkali present in the compound at the period when the soap-pan has become nearly filled by the repeated addition of oils and fats and lyes. He then adds common salt to the mixture, which by its superior affinity for water, as compared with that of the saponaceous compound, effects the decomposition of the emulsion, and causes this to be separated into soap combined with a definite quantity of water, but not having its full proportion of alkali, and a solution of common salt—which latter contains the glycerin of the fats or oils employed. The soap floats in a granulated state on the surface of the solution, which is then called "spent lyes," and should contain no free alkali.

After a few hours for subsidence the exhausted solution or spent lye is withdrawn from the soap-pan, from under the imperfectly-made soap, and is rejected as worthless.

The workman commences his second operation by the addition of some weak lye to the imperfect soap, and by boiling he brings the contents of his pan

again into a state of homogeneous mixture—called the "close state," as contradistinguished from the condition in which the soap is granulated and separated from the liquid contents of the pan; and if he has not already added his full complement of oils or fats, he completes the addition of them, adding also strong lyes until he finds the mixture has acquired a strongly alkaline taste. He then adds sufficient common salt to cause the separation of the soap from the alkaline solution, and boils the soap for some hours in the presence of the alkaline solution, to insure the whole of the fatty matter being combined with alkali.

If it is intended that the product should be framed as a "curd" soap, it is allowed to remain quiescent for a few hours, so that the lyes may subside; and the soap is then skimmed off and transferred to the "frames," in which it solidifies by cooling, and is then divided, by cutting with wire, into slabs and bars.

If the soap contains rosin as part of its acid constituents, it requires a further operation before framing. This consists in melting the curd soap (after the abstraction of the alkaline lyes from the lower part of the pan) with the addition of water, and boiling the mixture by steam or fire, or both steam and fire, so as again to produce a homogeneous compound containing an indefinite proportion of water, and allowing this compound to remain quiescent for two days, when a separation takes place, resulting in the elimination of a definite compound, containing in 100 parts about 65 of fatty acids, 6·5 of soda, and 28·5 of water. This forms the upper stratum of the soap-pan, underneath which is an indefinite compound, technically called "nigre," containing a much larger proportion of water.

When it is judged that the separation of these compounds has been well effected by subsidence, the upper portion, or definite compound, is usually taken out of the soap-pan by ladling, and transferred to frames to solidify by cooling. The residual portion, which contains an excess of alkali, as well as of water, is boiled up with salt and the addition of fatty materials, to form the succeeding boil of soap.

In Germany the kettle is charged with 190 gallons of soda lye of 30° B., and 2000 lbs. of the best melted suet. When the mixture becomes milky it is kept gently boiling for two hours, the source of heat is then removed, and after two hours' repose the lye is drawn off. The operations are continued as above described. When the soap forms by pressure clear solid scales between the fingers, the magma is cooled by throwing in some buckets of lye, and soon after it has settled drawn off clear. After the heat is withdrawn 9 or 10 gallons of lye are poured into the kettle, and when fusion is complete a trial of the paste is made with the spatula. If it runs from the lye water is added; if it does not run, it must be boiled a little longer, adding a bucket of water containing a third of its weight of common salt in solution, in order to effect the separation of the soap from the water. When this separation appears to be perfect, after an hour or more of repose, the water, which contains the greater part of the alkaline lye remaining from the first boiling (generally of a very deep bottle-green colour), is drawn off. The boiling is renewed with addition of about eight buckets of water, and when the incorporation is complete an examination with the spatula must be made to ascertain whether the soap runs from the water. If it does, water is added in small quantities until this ceases, and the pasty mass moves tremulously. To finish the operation the contents of the kettle are well boiled, and unless the soap has a bluish tint (in which case it must have another washing), the fire is extinguished, or the steam shut off, the kettle carefully covered, and the whole left to rest for a day or more, and then ladled off into the frames.

In the United States of America the following process is pursued:—The strength of the lye employed differs accordingly as the fat to be saponified is richer in olein or in solid constituent. The operation is commenced by pouring the lye into the boiling caldron to a third of its capacity. This is then heated to ebullition, and the oil is now poured in. The reaction is such that a magma is immediately formed. The proper formation of this magma is considered to be the most delicate and important part of the whole process; and if badly managed, a much greater quantity of lye is required to form the same weight of soap than otherwise would be. After pouring in the fat, the heat is decreased by opening the doors of the furnace; and when the mixture is complete, if necessary a further quantity of weak lye is added gradually, and with constant stirring during the addition, so as to insure thorough contact. The mass should remain homogeneous; the fat should neither rise to the surface nor descend to the bottom. If it rises, it is necessary to add more strong or weak lye, according to the capacity of the caldron. If the lye is in excess, a further quantity of fat must be added—always stirring briskly upon any addition of new material. The operation requires from eighteen to twenty hours for completion. It may, however, be greatly accelerated by throwing in the scrapings or the waste of soap already made. An excess of soda is recognized by the liquidity and transparency of the paste. The presence of a large proportion of common salt in the soda also prevents more or less the proper formation of the magma. When this is the case to any considerable extent, the use of soap scraps is indispensable. The next step in the process is the removal of the large quantity of water which was required for the ample saponification of the fat. This is effected by the addition of lyes containing common salt, and afterwards boiling the mixture from fifteen to twenty hours, constantly stirring during ebullition. When the mass opens in different places, the separation is esteemed complete. The fire is withdrawn, and the whole is now allowed three or four hours' repose, after which the settled waste lye is drawn off. A further quantity of lye, charged with common salt, is now added, and the mixture is gently boiled—the operator being careful to remove from the sides of the caldron any adhering soap, so that all portions may be in contact with the lye. The mass now acquires more consistence.

After some hours' repose, the settled waste lye is again withdrawn. Lye of specific gravity 1·10 = 20° Tw. is poured in, and the mixture is again boiled; by this it acquires a still greater consistence. After continued boiling for about three hours, it is allowed to deposit, and the waste lye is again drawn off. This operation is repeated once more, but with strong lyes, care being taken to stir the paste while being heated, and to allow only a gentle ebullition, so that the whole may form a homogeneous mass.

The soap at this stage begins to acquire firmness. The boiling with lye several times successively serves not only to complete the saponification, but to wash and purify the soap. That it may be perfect, it is necessary to repeat the operation four or five times. As soon as complete, the fire should be withdrawn, and the mass allowed to settle and become somewhat cool, and then ladled out and conveyed in buckets to the frames.

Framing.—When the soap paste has remained in the boiler a sufficient length of time to have become partially cool, it is ladled out into buckets or pails, conveyed to the frame-room, and poured into the frames to solidify.

The frames or *sesses* (Figs. 4 and 5) form when joined together a pile of rectangular inclosures,

Fig. 4.

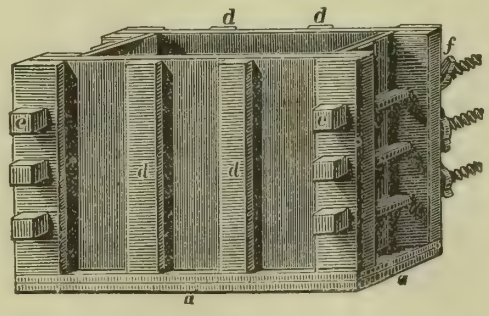
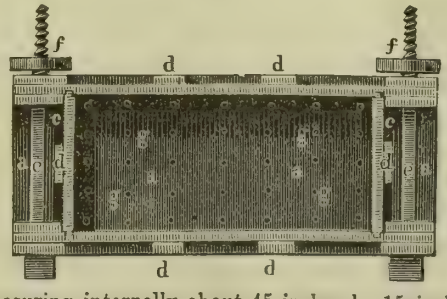


Fig. 5.



measuring internally about 45 inches by 15 inches. They should be very smooth, and so jointed as to fit closely together. When piled one upon the other, to the height of 3 or 4 feet, they constitute a tight square well fitted to receive the boiled soap paste. They are tightly bound together by clamps and screw rods, *e f*. The bottom, *a*, is made of two layers of planks; in the upper one are four grooves, into which the projections, *d d*, which support the sides, fit. The cross pieces, *c c*, support the ends. A cloth is spread over the bottom, to filter off the lye which runs out through the holes, *g g*.

Cast-iron frames, as a substitute for the above in the manufacture of yellow soaps, are of late introduction. These latter are formed of five rectangular plates, one for the bottom, two for the ends, and two for the sides, so arranged and fastened together as to form a well or reservoir of the same length and breadth as the wooden frames, and about 5 feet in height. These frames are put together and taken to pieces much more easily than those of wood, and the good conducting power of the iron considerably accelerates the cooling and solidifying of the soap. If the soap is allowed to solidify in the state in which it is run into the frames it has a rough granulated texture, and is extremely hard. It is therefore usual to mix a small quantity of water with it in the frame, and afterwards agitate the mixture with a wooden *paddle* or *crutch* until nearly cold. By this means it acquires a finer grain, and is not nearly so hard.

The soap having become cold and dry, and in a state to be removed from the frames, which may be known by gentle pressure of the finger making no impression, the iron screw rods which bind the frames together are remove', and each frame is lifted off the soap, which is left a compact mass of the size of the interior of the frame. This mass is then marked round with a kind of iron toothed *scribe* or *dentier*. The teeth are near or distant from each other accordingly as the blocks are desired of small or large size. The mass is then cut by means of a wire, inserted by the workmen in the track of the teeth, into slabs, and these are again subdivided into bars. The usual size of the bars is 15 inches long by $2\frac{1}{2}$ inches deep and broad.

Various machines have been devised for cutting the lumps of soap from the frames into slabs and bars. One much used in this country consists of a table, upon which the soap is placed at an angle, so that a hinged frame, provided with a number of wires fixed at the desired distances apart from each other, can be brought down upon it; the cut soap then falls through the hinged frame in regular bars.

Lesage has patented a soap-cutting machine, in which a cylinder, lying in a horizontal position, but capable of being raised into an inclined or vertical position for the convenience of filling it with soap, is closed in front by a plate perforated with a number of holes. The other end of the cylinder is closed by a piston, which, when urged forward by the piston-rod, presses upon the mass of soap, and forces it through the holes in the front plate, thereby moulding it into sticks whose transverse sections have the size and form of the holes. These are cut off from the cylinder by a rotating knife, or by a wire moving vertically up and down.

The bars, by whichever mode obtained, are next removed to the drying room, and piled upon one another crossways upon slatwork frames, made of wooden uprights and cross pieces, interstices being left for the free circulation of the air, which much facilitates the drying. The commoner kinds of soap

are frequently piled upon the floor without using any frame, but the lower bars of soap are apt to get misshapen from the weight of the superincumbent mass.

The bars of soap, when sufficiently hard, are stamped, either by a press with suitable box and die, or, in the case of bar soap, with a stereotype plate, which conveys its impression by being struck with a mallet.

White Soap—Curd Soap.—The material employed may be tallow or lard, or olive or well-bleached palm oil, or mixtures of these in almost any proportion. To produce 1 ton of soap, from 10 to 14 cwts. of tallow or olive oil are required. The process of saponification is conducted as above described, with but slight variation, attending more particularly to the complete removal of the *alumino-ferruginous* impurities of the lye, which otherwise impart to the soap a more or less intense colour. Their removal is effected by boiling the soap several times with fresh lyes, or by thinning out the soap with a little lye, and applying gentle heat, then covering the caldron carefully, and allowing it to settle. The upper strata of soap is afterwards ladled out and run into the cooling frames.

In place of this process, Anderson at this stage, instead of boiling out the head, and finishing as heretofore practised, pumps out or draws off the strong lye on which the materials have been boiled, and then adds weak lye or water in successive portions, and boils the whole until the mass assumes a proper appearance for fitting. The mixture is now allowed to stand at rest for from twenty-four to forty-eight hours, or until the *nigre* or imperfect portion of the soap is deposited. This latter may then be separated, either by pumping it off from under the purified compound into an adjacent kettle, or by removing carefully the upper stratum of purified soap by means of ladles or buckets.

Whichever method be pursued, the cleansed material must now be treated with the proper finishing lye for curd soap, which being added, the whole is boiled until the soap becomes of sufficient consistence to be transferred to the cooling frames. When the materials employed in the production of this soap are very impure, the fitting or purifying process as above described is repeated one or more times; in which case, after the first separation of the imperfect soap, the remaining partially-purified material is treated with a lye only of moderate strength, instead of the ordinary finishing lye, and the whole is boiled with weak lye or water until sufficiently diluted to allow the proper performance of the fitting process—after which, time is allowed for deposition, the imperfect soap is again removed, and after the addition of the finishing lye, the remainder is boiled to a curd as before. The further treatment of the separated *nigre* or imperfect soap, and its conversion into mottled soap, is effected by adding to it in an ordinary caldron the usual finishing lye for a mottled soap, and boiling until it is of proper consistence to be removed to the frames. The quantity obtained from one charge of soap by the fitting or purifying process is not enough to be conveniently boiled by itself; it is therefore set aside, and six or more batches operated upon at one time.

The average composition of ordinary white tallow soap is—of alkali, 1 part; of fatty acids, about 9 parts; and 5 to 8 parts of water. In England by far the greater quantity of curd soap produced is made from tallow or mutton suet and soda only. Some manufacturers, however, substitute for one-fourth of the tallow as much lard or olive oil, and a soap is produced greatly superior in quality, and less liable to change by exposure. Soap made solely of tallow is, besides, inconveniently hard, and very difficult of solution. In France and on the Continent, when tallow is saponified, olive oil is always added in the proportion of 20 to 25 per cent. of the oleaginous material. In England lard is not unfrequently used as the softening agent; and when applied in about the same proportion, answers every purpose, while it has the advantage over olive oil that it does not detract from the whiteness of the soap. English white or curd soap is largely used by the cloth manufacturers of Yorkshire, and the lace and stocking bleachers of Nottingham. Tallow is not saponified to a very considerable extent on the Continent; but in its stead, olive oil mixed with about one-fifth of rape oil is used in the manufacture of hard soaps. This addition of rape oil is always resorted to, because olive oil alone yields a soap as hard and compact, and as difficultly soluble, as soap made wholly of tallow and alkali. This, however, is not the case with rape oil, and other oils of a similar nature—that is, such oils as become thick and viscid by exposure—experience having demonstrated, though the reason is as yet unknown, that the oils which turn viscid the soonest by exposure, yield with soda softer soaps than those made with oils which, like olive oil, remain long limpid under the influence of the air. The admixture of rape oil with olive oil has therefore the effect of modifying the degree of hardness of the soap, just as when lard is saponified in conjunction with tallow.

Yellow Soap.—This variety of soap differs from other kinds in containing rosin. This substance, as previously observed, enters into combination with the alkalies, producing a detergent compound soluble in water. The combination, which cannot be called saponification, takes place equally well with carbonated as with caustic alkalies. The soap separates on the surface when an excess of carbonate is used, or in the presence of common salt, as a thick, slimy, brown mass, smelling strongly of rosin, and containing 15·8 per cent. of soda. Besides the rosin, common fat or inferior tallow, palm oil is also used to a considerable extent. The usual proportion of palm oil and rosin are $3\frac{1}{2}$ parts of the former to 1 of the latter; sometimes the proportion is still greater, and the soap produced is then soft and dark coloured. When the saponification of the oil is nearly complete—that is, at the last charge of the lye—the rosin is introduced in a state of coarse powder, and well

mixed with the soap by agitation. The mixture is then boiled for some hours; a small quantity of lye being added from time to time, if necessary, to preserve an excess of alkali until the soap is completely formed, when the lye may be withdrawn and one or two waters, or else weak lyes, applied successively with agitation for the purpose of washing and purifying the soap. The resinous scum being removed for another operation, the soap is conveyed to the iron frames to solidify. Yellow soap usually contains, to 1 part of soda, from 10 to 11 parts of oily acid and rosin, with from 24 to 30 per cent. of water. This communicates to the soap a viscid consistence which is not altered by long exposure to air. According to RICHARDSON and WATTS, the best plan of preparing the soap is to saponify the rosin and tallow separately, and to mix the two soaps in the boiler, where they are retained in a state of ebullition for some time, until a uniform mixture has been effected; salt is then to be added and the soap brought to the moulds. It is not advisable to mix the separate soaps in the moulds, though this plan is sometimes adopted. The soap is finished when a cooled sample is of the right consistence, and does not leave a film. If it contains a large proportion of water, it has just the same appearance as when it contains only a small proportion. When anything like 50 per cent. of water is present, it has been added while the soap was in the frames for the purpose of fraud.

If tallow or other grease be employed in the manufacture of yellow soap, instead of palm oil, the following is the mode of procedure:—2000 lbs. of the oil or fat, 600 lbs. of rosin, and from 150 to 175 gallons of soda lye of specific gravity 1·075 to 1·150 = 15° to 30° Tw., are run into the boiler, and when the whole is melted, the mixture is heated to ebullition, stirring carefully all the time to prevent the rosin adhering to the bottom and sides of the caldron. Should the mass begin to swell out, the heat must be decreased. The first boiling should be continued not more than two or three hours, on account of the facility with which the combination of the fat and alkali is effected. After six hours' repose the exhausted lye is withdrawn, and fresh substituted, and the whole is again boiled for three hours or more. This is repeated, and the boilings are thus continued, day after day, until the soap has acquired a proper consistence, which may be ascertained by taking a small portion, and when cool, squeezing it between the thumb and finger. If hard thin scales are formed, it is finished, and after having boiled briskly, the fire is removed; but if greasy, clammy, and soft, it is not perfect, and it is necessary to add more lye and reboil. The soap is now to be cooled by adding three bucketfuls of lye, and after two hours the liquor is withdrawn. Six or eight bucketfuls of water are now added, and the whole is again briskly boiled, stirring constantly until the soap is melted. A little of the boiling paste is now removed on a wooden spatula, and if it run clear from the lye, more water is added, and the boiling is continued. If it should not run, too much water has already been added, and a half pailful of strong solution of salt must be thrown in.

The most delicate part of the operation is that of boiling, and it therefore requires particular attention. When it is complete the soap should, when a portion is taken on a spatula, and the latter is held in an oblique position, shake and disperse tremulously, as would a body of gelatinous consistence. When it acts thus, the fire may be withdrawn, and the soap considered as finished.

Rosin soap can be prepared from curd soap by adding to it about 25 per cent. of rosin, then adding 2 to 4 per cent. of carbonate or bicarbonate of soda, and 1 or more per cent. of alum or aluminium sulphate; the whole being boiled with water till perfect combination is effected. To prevent the rosin from precipitating, about 2 per cent. of dilute sulphuric acid (1 part of acid to 9 parts of water) is stirred into the mixture.

In France yellow soap is produced by a similar process to that for other kinds of common soap, adding, however, at the commencement of the operation 15 to 20 per cent. of rosin. Some manufacturers make a soap with but 5 to 10 per cent. of rosin, and this being lower priced than soap made entirely of grease, has a more extensive sale, and is preferred especially for domestic purposes. By its property of dissolving more readily in sea-water than other soaps, it is also well adapted for use on shipboard.

The common brown soap is made in the same way as described above, but a greater proportion of rosin is used; the common kinds of grease, such as soap fat, bone fat, &c., are substituted for the tallow, either wholly or partially.

Rosin soap has a yellow colour when palm oil is used; otherwise it is apt to be brown. It is very firm, rough to the touch, and translucent. The best quality when cut shows a fibrous structure. It always retains the smell of rosin.

Meinecke's Process.—The soap-pan is constructed with a still head and cooling worm, in order to condense the oil of turpentine which is given off from the rosin, which is used in the form of white turpentine; 1000 lbs. of white turpentine are melted in the kettle by steam with 800 lbs. of tallow or other fat; and when the mixture reaches 108° Fahr., 800 lbs. of caustic soda lye, containing 30 per cent. of dry soda, are added by slow degrees. The saponification is very rapid at this temperature, the acids of the rosin and fat being completely neutralized and converted into liquid melted soap. The essential oil of turpentine is set free at the same time; and in order to promote its evaporation salt or brine is added. The head being then luted on the pan and the worm fitted to it, the mixture is brought to the boil, when steam and oil of turpentine pass into the worm, and are there condensed. When all the essential oil is distilled over, the soap is finished in the usual way.

Dunn's Process.—Steam is used to heat the lyes, whilst air is forced below their surface by means of a pump; the saponification is thereby greatly accelerated. Into each of the ordinary boiling

caldrons a circular ring of pipe, of about 1½-inch bore, and perforated with small holes, is fixed in the well of the kettle, just below the flange or joint, keeping it sufficiently off the bottom to allow a stirrer to be used to scrape the bottom when necessary. The pipe is supplied with atmospheric air from a cylinder blast, or other suitable forcing apparatus, and is connected with the latter by means of a pipe attached thereto, and rising up to the top of the kettle, where it is furnished with a stop-cock and union-joint, for the purpose of connecting or disconnecting the parts of the pipe within and without the copper.

For a good yellow soap, 90 gallons of lye of specific gravity 1·14 = 28° Tw. are run into the caldron. The fire being kindled, the caldron is charged with 2050 lbs. of grease; and as soon as the lye is at or near the boiling point, the blast is commenced, keeping up a brisk fire, so as to continue the materials in the kettle as near ebullition as possible. When the lyes are exhausted, an additional quantity is gradually added until the grease, oil, or fatty matter is taken up; 550 lbs. of rosin are then added—a bucketful at a time, with more lye occasionally, until 300 gallons of the strength above-mentioned have been used, keeping the blast in action the whole time, and the contents of the kettle as nearly boiling as possible. When the whole of the rosin is melted, and thoroughly incorporated with the saponaceous mass, and the strength of the lyes taken up, the blast should be stopped, and the contents of the boiler briskly boiled, and then allowed to rest, that the spent lyes may separate and deposit. These being now drawn off, the soap is then brought to strength by fresh lyes, as in the ordinary process of soap-boiling. During the operation of the blast the soap must be kept in an *open* or *grained* state; and for this purpose salt or brine is to be added when necessary. Experience has shown that it is better not to make a change of lye during the operation of the blast, when lye of the strength above-mentioned is used; but if weaker lye is employed, one or more changes may be made. It is found desirable, also, that the soap should be kept in a *weak* state during the passage of the streams of air through the materials, otherwise it is apt to swell up, from the air hanging in the grain; and this is found troublesome to remove, requiring long boiling. If dark-coloured materials are used, it is well to keep the blast in operation three or four hours after the rosin is melted, provided the soapy mass is kept *weak* and *open* or grained.

Normandy's Process.—By this process a soap is obtained from the cheaper oils, possessed of detergent properties and a degree of hardness approaching to that obtained by the employment of the more valuable fats and oils.

When the soap is made in the usual manner, and is ready to be cleansed, there is to be introduced and crutched into it a certain quantity of neutral anhydrous sulphate of sodium, or of hyposulphite of soda, or of the two salts conjointly.

The "salt-cake" is treated with a quantity of hot water, less than is necessary to dissolve the whole of it, and to the saturated solution thus obtained as much solution of caustic or carbonate of alkali is added as is necessary to impart to the liquid a faint alkaline reaction. This addition is made not only to saturate any free acids that may be present, but also to remove the ferric oxide always contained in crude salt-cake, and which, by this treatment, will be precipitated. When this precipitate has completely subsided, and the supernatant liquor is perfectly clear, as much of the latter is added to the soap paste as is necessary to confer upon it the requisite degree of hardness when cold—the particular quantity varying according to the nature of the fat or oil saponified, or to the proportion of rosin present. The mixture of salt-cake solution and of soap are thoroughly incorporated by stirring or crutching, continuing the agitation until the mass has become so hard that the stirring can be no longer practised. When hyposulphite of soda is used, it should be dissolved in very little hot water, and the solution added to the soap exactly as above described.

MOTTLED SOAP—MARBLED SOAP.—In the manufacture of this variety of soap, the same kinds of materials are used as for white soap, and its different appearance arises from the different mode of treatment of the soap, after the completion of saponification. By a reference to the general process of soap-making given above, it will be observed that even after the complete formation of soaps, that is, when the whole of the oil or fat used is decomposed, and the oily acids have entered into combination with alkali, the soap still requires further treatment before it is brought into a marketable condition. It exists now in the form of immovable globules, and it is necessary to cause these to coalesce into a homogeneous mass. This is effected by a process termed *fitting*, which consists in the fusion of the contents of the boiling caldron in a weak lye or in water, and afterwards boiling the whole for a longer or shorter period, according to the kind of material operated upon, the mass being prevented from boiling out of the copper by dashing shovels into it, so as to break the froth and favour evaporation. During this process in making white or curd soap, the more or less coloured impurities of the materials, termed *nigre* or *nigger*, fall to the bottom; but in making mottled soap, the mixture is left in a thick or viscid state, so that the impurities cannot subside, and is transferred to the frames in this condition. To produce a good marbled soap, it is necessary that this latter operation be very carefully conducted; as, if too great a quantity of liquid be added, or if the mixture of soap and water or weak lye cools too slowly, all the colouring matter falls to the bottom, leaving the upper stratum of soap perfectly white, while, on the other hand, if it becomes too quickly cold, the soap remains in the granular condition. In some cases the mottling is produced, or at least the proportion is increased, by sprinkling on the surface of the soap, after being boiled with the last service of lye, a small quantity of very strong sulphuretted

lye, which produces the mottling by filtering slowly through the mass of soap. At Marseilles and other places where olive oil is used in making soap, a quantity of sulphate of iron is added; in which case the mottling is produced both by the black sulphide of iron and by the oxide of iron—the red portion—which latter combines with fatty acids, producing a true ferruginous soap. The quantity of copperas requisite is about 18 ozs. to 450 lbs. of oil or fat. It is added first mixed with weak lye, and should be poured in during the coction of the soap, and before it has acquired too much consistence. When the soap is ladled out of the boiler, it is of a uniform slate tint; but as it becomes cool, the portion containing the iron solution separates into nodules, and by the trickling of the excess of lye through the mass it becomes *mottled*. By varying the proportion of sulphate of iron a tint is produced of a lighter or darker hue. Soaps containing this have a rusty colour, owing to the oxidation of the iron, and this shade may be deepened by the addition of venetian red or colcothar, into the particular tint to which the French apply technically a term signifying *hidden red*, and which upon the deep blue produces the appearance of marble, as seen in the variety known as *castile soap*. This peculiar tint may be communicated as well before as after the true marbling; for which purpose it is necessary to thin out the colcothar with water, and in adding it to incorporate it well with the soap. Generally, in the preparation of mottled soap, less care is exerted in the choice of materials than for white soaps, and the heterogeneous mixture of fatty substances known as *kitchen stuff* usually forms one of the materials.

A well manufactured mottled soap cannot contain more than 33 to 36 per cent. of water, whereas genuine curd soap contains 45 per cent., and yellow at least 52 per cent. The mottling being due to the presence of sulphide of iron held in a state of suspension and demi-solution, it is evident that addition of water would cause the colouring matter to subside, and a white soap would result. The addition of water, technically "fitting," is in fact the process used to obtain colourless soap, whether it be curd or yellow.

Cocoa-nut Oil Soap—Marine Soap.—Cocoa-nut oil is very easy to saponify, and is used to a considerable extent in the manufacture of white soap, as well *per se* as in admixture with other oils and fatty matters. The disagreeable odour is removed most effectually and conveniently by boiling in a wooden vessel by means of steam with a mixture of 6 lbs. of sulphuric and 12 of hydrochloric acid to each tun of oil. The oil so purified is heated in the boiling caldron, with the addition of a portion of olive or some other readily saponifiable oil or fat, and the soda lyes are gradually introduced in the usual manner. Towards the conclusion of the process of saponification, a quantity of caustic potash lye is thrown in, and the boiling is continued as long as may be necessary. The soap thus formed requires, for its separation from the lyes, a much larger proportion of salt or other saline matter than the soaps formed of tallow, palm oil, or olive oil; hence the usual mode of proceeding is not followed in the production of this soap. The principal distinction between cocoa-nut oil and other oils and fats is, that while the latter are most readily saponified by weak lyes, cocoa-nut oil is quite unacted upon until the lyes have obtained a considerably higher degree of concentration; saponification then suddenly commences, and proceeds with extraordinary rapidity. Only the strongest soda lyes are employed in the production of cocoa-nut oil soap, and by taking pure and perfectly caustic lye, the use of salt in purifying the soap is dispensed with. Pure cocoa-nut oil hardens much too quickly to exhibit any distinct formation of curd, and is consequently incapable of marbling of itself; it is very white, translucent, exceedingly light, and forms a good lather, but has always a more or less offensive smell.

An important property of cocoa-nut oil is its power of combining with more water than can ever be incorporated with tallow soap, and this property frequently leads to dishonest practices. Cocoa-nut oil actually produces no greater quantity of soap than an equal weight of tallow; but the soap from the former can easily be made to absorb one-third more water or lye, and at the same time exhibit no want of consistence or softness, as would be the case with other soaps.

Cocoa-nut oil is not usually saponified alone, but is added to other oils for the purpose of producing quickly solidifying soaps containing a large proportion of water. When equal parts of cocoa-nut oil and tallow are used, the soap has the smell of common tallow soap. The boiling is continued until a specimen exhibits the proper consistence under the thumb. Tallow itself could not be saponified under the same conditions; but the saponification begins with the cocoa-nut oil, and the tallow is then saponified by means of the presence of cocoa-nut oil soap.

The different varieties of this soap are marbled artificially. The blue or red colouring matter is rubbed up with a little of the soap, or better, with a separate portion of good cocoa-nut oil soap, until the whole acquires a red or blue colour. This is then placed in alternate layers with the colourless soap; and by stirring the mass together streaks and veins are produced in all directions.

A mottled soap is also manufactured from cocoa-nut oil and palm oil, wherein the mottling is so perfectly effected by means of ultramarine and black or brown oxide of manganese, that it is impossible to distinguish it from the true mottled soap: 80 cwts. of palm oil are made into soap in the usual way, and the spent lye pumped away, so that the curd is left perfectly free; then 32 cwts. of cocoa-nut oil, 60 cwts. of lye at 20° B. added, and by slow degrees 14 cwts. of lye at 14° B. The whole is then boiled till complete saponification takes place. The colouring matter, 6 to 7 lbs. of ultramarine (or whatever pigment may be used), is well stirred into weak lye, and poured into the soap through the rose of a watering pot; the whole is then boiled for half an hour to an hour, and the

soap is then transferred to the ordinary wooden or iron frames (in the latter case surrounded with matting, so that the soap may not cool too quickly). The above proportions yield 212 cwts. of soap.

SILICATED SOAPS. — Many varieties of soap are met with in commerce termed silicated soaps. They are produced either by the addition of silica itself or an alkaline silicate to the soap paste, just before cooling and solidification.

Soaps are also thus styled which contain pipe-clay, fuller's earth, &c. These ingredients are reduced to powder, mixed with their own weights of dry soda ash or pearl ash, and thoroughly incorporated with the soap by crutching or stirring, while it is still in the state of paste. The mixing must be completed before the pasty soap cools.

Sand Soaps.—Sand soaps differ from silica soaps, inasmuch as in the latter the admixture has been prepared artificially, while in the former common white sand is the silicious ingredient, and the only preparation it has undergone is finely sifting. In the preparation of sand soap, the finely-sifted sand is added to ordinary white soap and thoroughly incorporated with it while in the pasty condition, in the proportion of 7 or 8 per cent.; and as soon as the mass has cooled, it is taken from the frame and cut into tablets or moulded into balls.

When the silicious ingredient is flint or quartz, the calcined material is reduced to nearly an impalpable powder by wet grinding with horizontal stones. The powder obtained is thinned out with about 20 per cent. of water, and then boiled with caustic soda lyes of the strength above-mentioned for eight hours, or until it becomes a homogeneous mass. In this condition, in which it is technically termed *detergent mixture*, it is ready to be mixed with the soap paste.

Gossage's Process.—Of the three silicated soaps, the first that claims mention is that invented by W. GOSSAGE. It consists in the introduction into soaps prepared from fatty or resinous materials of a highly concentrated solution of silicate of alkali. The process for the preparation of this silicate, termed also *soluble glass*, is described in the specification as follows:—When soda is used as the alkaline solution to be combined with silica, 9 parts of soda ash containing 50 per cent. soda are mixed with 11 parts of clear sand, and the mixture fused in a reverberatory furnace, provided with a tap-hole through which to allow the finished product to run off. Sufficient heat is to be applied to the mixture, stirring from time to time until combination has been effected; the product is then drawn, and received either in metallic moulds, or in moulds formed of damp or moistened sand. The charge for a furnace having a bed or sole measuring 60 square feet, is about a ton of the mixed sand and alkali, and each charge requires four or five hours to be properly fused and combined. For the preparation of silicate of potassium the proportions are equal weights of crude carbonate of potassium and sand, and these are melted exactly as in the production of silicate of sodium. It is always desirable to use such proportions of alkali and sand for the production of the silicate, that the latter may be almost wholly soluble in water; when the alkali is deficient, however, this is not the case, and to obtain perfect solution it is necessary to use as the solvent a solution of caustic soda or potash.

The solution of the perfect silicate may be effected simply by grinding the latter to powder, and agitating this in a pan containing boiling water; but a much preferable method of dissolving is by the employment of an apparatus consisting of a vessel formed of iron plates, or other suitable materials, which vessel is fitted with a perforated diaphragm or false bottom placed about mid-way between top and bottom. The silicate, first broken into small lumps, is placed upon the false bottom, and hot water is introduced into the vessel to a sufficient height to cover the pieces of glass to be dissolved. Steam is then introduced into the water so as to maintain the latter at a high temperature.

As the glass dissolves, it communicates additional gravity to the water, and the heavier solution descends in the vessel whilst the lighter fluid rises, and coming in contact with the glass also dissolves it, and acquiring density again descends. In this manner a continued circulation of the fluid takes place, and the glass becomes nearly all dissolved, yielding a strong solution.

After allowing undissolved matters to deposit, the solution is transferred to a cast-iron evaporating pan, and by the application of heat concentrated until of specific gravity 1·450, when it becomes viscous on cooling, and is then in a condition to be added to the soap. When the solution of the silica is to be added to a soda soap, the latter, prepared in the usual manner, is to be transferred from the caldron into a tub or pan, termed the mixing vessel, capable of containing about 14 cwts. of soap, and the viscous solution of silicate of soda is to be added in such proportions as to yield the particular quality of soap desired to be produced; and the mixture is then well agitated by means of crutches or paddles. The soap and the viscous solution should be each at such a degree of heat that the mixture, when formed, may be at a temperature of 160° Fahr., and the agitation is to be continued until the temperature is reduced ten degrees, that is, to about 150° Fahr. The mixture is then transferred to the cooling frames, and agitated therein by means of crutches, until it becomes of such consistence as to render its continuance no longer practicable.

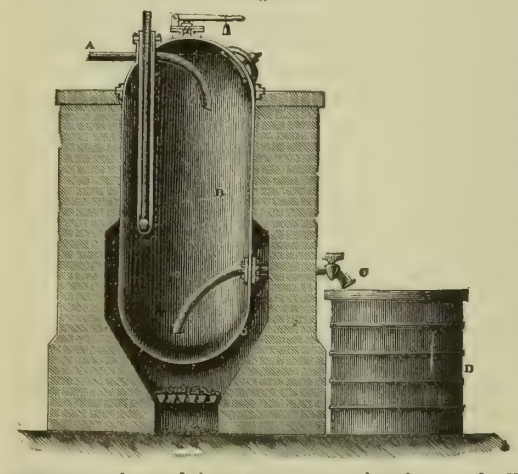
For admixture with soft soap, the soluble glass is formed by the fusion of a mixture of sand and potash, as previously mentioned, for the preparation of a silicate of potassium. This is dissolved, and after concentrating the solution to the viscous condition, it is mixed with the soft soap, exactly as described in the case of soda or hard soaps. As the proportional amount of alkali contained in a mixture of soap with soluble glass is greater than that contained in the unmixed soap — if it is desired to reduce this amount, as the excess of alkali may be injurious for some purposes to which the soap may

be applied, it is effected by the addition to the solution of the silicate of sulphuric or hydrochloric acid, previously to its reduction to the viscous condition. The mixed silicated soaps may be obtained of any requisite degree of hardness by the greater or less concentration of the solution of soluble glass. The compound soaps produced by the above process are possessed of valuable detergent properties, independently of the real soap contained in them.

Sheridan's Process.—Calcined flint, quartz, or sand is used for the production of soluble glass. If sand is the silicious ingredient, it is mixed with carbonate of soda in the proportion of 1 part of sand to 3 of soda, and the mixture is then fused in a reverberatory furnace. The product of calcination is drawn out into water and dissolved by the aid of heat. Thus far the process resembles that of W. GOSSAGE. SHERIDAN, however, now passes a current of carbonic acid through the solution of silicate of soda, whereby the silica is displaced from combination and precipitated in a gelatinous form. From this the liquid containing the soda, reconverted to the state of carbonate, is withdrawn, and evaporated to dryness for use again; the precipitated silica is mixed with caustic soda or potash lye of specific gravity 1·1515 = 30° Twaddell, and boiled for eight hours, with constant stirring, until it becomes a homogeneous mass.

Dunn's Process.—The apparatus employed is represented in section, Fig. 6. The boiler, B, should be furnished with a man-hole, safety valve, a thermometer plunged into a mercury chamber, and all the ordinary appendages of such an apparatus. A is the feed-pipe, and C the pipe through which to discharge the finished product. The crushed flint or quartz to be combined with the soap is mixed with caustic soda or potash lye, in the proportion of 1 cwt. of silica to 100 gallons of lye of specific gravity 1·16 = 32° Tw., and introduced into the steam-tight boiler. The fire is then kindled, the valve being so regulated as to allow the temperature of the materials to rise gradually to about 310° Fahr., or at a pressure of 50 to 70 lbs. to the square inch. When it has remained at this temperature for about three or four hours, the contents are discharged and cooled down. The solution of silicate of potassium or sodium thus obtained is added in the proper proportion to the soap paste, either in the caldron or frame after the saponification is complete, and before the soap becomes too cold.

Fig. 6.



J. P. WAY'S *silicated soap* is prepared from a silicious earth found in Surrey, which contains much soluble silica. A steam pan is used. Into this a soda lye is run of about 18° Tw. The silicious earth, ground to powder or broken into small pieces, is then added by slow degrees until the alkali has taken up as much as it will dissolve. The heat is now withdrawn, and the undissolved earthy matter allowed to settle. The clear liquor is run off, and the sediment washed.

In making soap the proportions used are 11·5 per cent. of palm oil, 11·5 per cent. of cocoa-nut oil, 30·6 per cent. of soda lye of 36° Tw. The whole is boiled until the soap becomes stiff, upon which 44 per cent. of silicate of soda (prepared as just described) of 36° Tw. is added, and the boiling continued till the soap becomes thin and limpid, at which stage 2·4 per cent. of common salt is added, and the soap boiled for three or four hours longer. It is then ready to cleanse. This may be done at once, or after it has been allowed to stand for a few hours. If open steam is used—that is, steam blowing into the pan—the silicate solution and lye require to be somewhat stronger.

MARSEILLES SOAP.—This variety of soap is produced by the saponification of olive oil alone. The process does not materially differ from that described for white soap. The duration of the operation is longer or shorter according to the quality of the oil. Some manufacturers use, in the fabrication of this soap, a certain proportion of poppy, or other seed oil, with the olive oil; and the addition is rather beneficial than otherwise, as the soap produced is less hard, and consequently more easily applicable to detergent purposes. It is at present manufactured on a considerable scale in this country.

The value of this oil for soap-making increases as it is less coloured, and is in proportion to the amount of stearin it contains. The oils of Provence are most highly esteemed.

The lyes used are of three strengths, the weakest is 4° to 5° B.. the next strong 10° to 15° B., and the strongest 20° to 25° B. These lyes are kept in brickwork cisterns until required for use. Pure soda is used for the first lye boiling, in order that no common salt may be introduced at this stage.

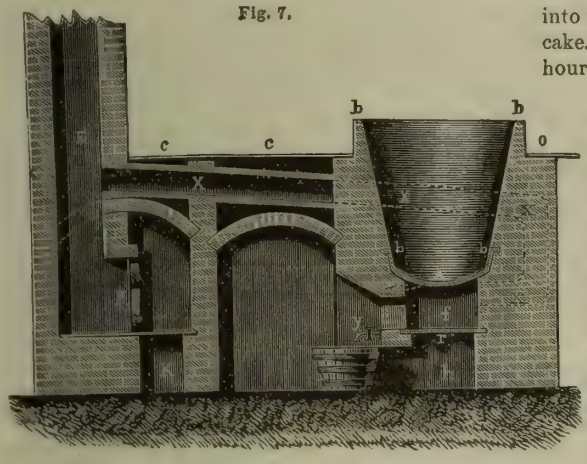
The saponification is begun in two boilers at the same time, and the contents of both are joined for the finishing operation.

The arrangement of one form of the apparatus is shown in the annexed section, though steam pans are now sometimes employed if superheated steam is accessible.

The bottom of the boiling pan, A (Fig. 7), is of cast iron or copper; the sides are composed of brickwork, lined with cement, to resist the action of

water. The upper part, *b b b b*, which never comes into contact with the fire, and is intended to afford space for the soap to rise, expands in the form of a cone. The fire-place, *f*, is separated from the ash-pit, *h*, by the grate, *r*. The fire, after having heated

Fig. 7.



the bottom of the pan, passes by the flue, x x x, half round the side of the pan into the chimney, E. This is accessible for the purpose of cleaning by the door, P. The soot is thrown into the pit, K. A tube, with a cock, *y*, leads from the lowest part of the pan for the removal of the lye. The whole of the pan is sunk into the floor of the boiling house in such a manner that the brickwork of the upper part projects about 3 feet above the ground.

These pans are made to contain 240 cwts. of soap. The upper part is frequently constructed of oak staves, and sometimes a siphon is used instead of the cock and tube, *y*. The violent ebullition of a direct boiling is considered so advantageous as to counterbalance loss from occasional burning.

A boil of 120 to 160 cwts. of oil passes through three stages. At first a lye of from 8° to 11° B. is used. This is prepared in the boiler by mixing the first and last lyes above mentioned. As soon as this has come to the boil the whole of the oil is run in, and soon an emulsion is formed, which thickens as the evaporation of the water proceeds. If oil floats on the surface more lye is added. The soap must remain in solution; if it separates an extra quantity of weak lye is added: 6 to 8 lbs. of green vitriol are added for the purpose of mottling. The next stage is the addition of salt, or rather a strong lye containing salt. This is poured gradually into the pan, with constant stirring until the soap begins to congeal and separate in flocks. In the course of three hours the lye below it may be drawn off. The soap is next scooped into one pan to finish: 280 gallons of saline lye of 18° to 20° are added and the boiling proceeded with. The further assimilation of soda is now dependent upon the concentration of salt lye in the pan. When the lye appears no longer caustic, that which is in the lower part of the pan is drawn off and replaced with fresh soda lye. The operation is repeated from four to six times, during which the soap acquires great consistence, and the alkalinity of the lye is less easily destroyed.

At length the lye retains its alkalinity, and the soap begins to boil in a jerky fashion; the frothy mass forms itself into granules, and the smell of oil is no longer perceptible. The curd when pressed into the palm of the hand should form a firm granular cake. The fire is kept up for from ten to eighteen hours after the last portion of lye has been added.

The curd has a slate colour, produced by the sulphide of iron and iron soap. In order to disseminate the colouring matter as veins through the soap, the consistence of the soap (at present too great) is diminished to the proper amount by sprinkling the surface of the mass with weak lye, at the same time that workmen rake and stir it about with stirrers in such a manner as to bring the lower parts of curd to the top, thus equalizing the lye and colouring matters.

The soap is then scooped into moulds, when in eight or ten days it cools down to mottled soap. The reddish tint is due to exposure to the air.

Soft Soap.—This variety of soap differs in many essential particulars from those already described. The alkali used in its production is potash, and the oil, either in whole or in part, a drying oil, as that of hemp seed, poppies, &c., or a fish oil, as whale or seal oil. The reaction of potash upon fats and oils is precisely the same as in the case of soda.

Soaps with potash are, however, manufactured on an entirely different system to those of soda or hard soap. In the latter, the soap is withdrawn from the lye when only a portion of the oil has been saponified, and fresh lyes are added until saponification is complete.

In the production of potash or soft soaps no lyes are separated during the whole course of operation; the only object being the combination of the potash with the fat or oil. Potash soap, therefore, of course contains the whole of the base of the oils or glycerin, which is expelled from combination by the stronger base, as well as the impurities always existing in the lye, as carbonate of and caustic potash, chloride of potassium, sulphate of potassium, and in small quantities many other salts, which in the manufacture of hard soaps are removed in the exhausted lyes. Potash soap, also, always contains a much greater proportion of water than hard soaps, the quantity being in the majority of instances from 50 to 60 per cent. If desired, the glycerin of the fat and saline impurities of the lye might easily be removed by the application of strong lyes towards the completion of the process, but on the large scale such a system is never pursued. A much larger proportion of alkali is consumed by a given weight of oil or fat, when saponified by potash, than when soda is used, 1 part of pure potash being taken up by from $4\frac{1}{2}$ to 5 parts of oil; and hence the quantity of real soap produced from a given weight of oil or fat when saponified by potash is considerably greater than when the alkali used is soda; and this quantity is still further augmented by the large proportion of water, together

with the glycerin and saline impurities always contained in the lyes, and which, as above stated, are not removed from the soap.

From the great analogy which exists between soda and potash compounds, it would be expected that potash soap would be separated from its solutions by chloride of potassium, as soda soap is by chloride of sodium. This, however, is not the case, as when to a solution of potash soap, procured by treating oils or fats with caustic potash lyes, a considerable quantity of chloride of potassium is added, no separation of soap takes place; the salt dissolves in the soapy mixture, and the solution remains clear. Potash soap can only be separated from the lyes and eliminated glycerin by adding strong potash lyes after the soap is complete, and the excess of alkali and the glycerin may then be allowed to subside, and subsequently be more completely removed by placing the soap to drain. On the large scale, however, as before observed, soft soap is never separated as above; the soap solution is boiled down until homogeneous and of a proper pasty consistence.

Soft soap is therefore practically a mixture of potash soap with more or less caustic lye, forming at ordinary temperatures a thick transparent jelly. Addition of salt converts it into hard soda soap.

The process of manufacture of soft soap is as follows: the proportions of oil and lye being regulated according to the strength of the latter, and the qualities operated upon at once varying with the greater or less capacity of the boiling caldron. The larger the caldron the better and more economical. To be properly proportional, the diameter should always be greater than their depth, and the pan should be only half filled with material, as the soap when boiling swells up considerably. In some soaperies the whole of the oil and tallow is introduced at once, together with a portion of the lye, and the remainder of the lye is added after some hours' ebullition; in others, both the oil and lye are introduced gradually. The lye should indeed always be gradually added, and in small quantities at a time, spreading it superficially over the whole mass. As soon as the two clear liquids, separately introduced, unite together, the whole becomes much thicker, and in some cases boils quietly, but in others swells up into froth. In the latter case it must be thrashed with a stirring pole, and dosed with a sufficient quantity of lye to lessen the commotion and prevent loss of the material by running over. The caldron requires to be constantly watched while over the fire. If too much lye is added at the commencement, no union is effected between the oil and the alkali; and if the lyes are too strong they seize on the oil too rapidly, and instead of becoming thick and viscid, the mass becomes clotted. This latter inconvenience may be remedied by adding lyes of a lower degree of strength. If the lyes are not sufficiently strong, combination ensues so tardily that part of the superabundant water must first be expelled by evaporation before a perfect union between the oil and alkali can be effected. The lyes used at the commencement of the operation are of specific gravity 1·06 to 1·08.

When combination is perfect and the great foamings have subsided, the pasty mass should become clear and transparent, and free from clots or granules, and no acrid taste should be perceptible. To ascertain if this be the case, a small sample is taken out and cooled. If it should not be of proper consistence and free from opacity, the boiling is continued, and after some time another sample is taken, and so on until the soap is properly finished. If the test sample thickens on cooling, has a brown colour, is perfectly homogeneous, and is not ropy when worked between the fingers, the soap is finished, and the fire should at once be withdrawn. A fair criterion of the quality of the soap is furnished by a peculiar phenomenon observable during its cooling; a little opaque zone forming around the test-portion taken from the caldron and placed on a glass plate for an assay, indicates perfect saponification, and is called *strength*. The absence of this zone denotes a deficiency in strength; and when it vanishes soon after having made its appearance, the soap is said to have *false* strength. When it comes in the best form the soap is perfect, and may be secured in that state by removing the fire, and then proceeding as subsequently directed.

To allay the foaming and render the finished soap fit to be transferred to the barrels or casks without endangering its detergent quality or diminishing its causticity, the soap should be cooled as rapidly as possible. For this purpose a quantity of ready-made soap—a ton or more, according to the size of the caldron—is added to the hot mass. This, in melting, rapidly abstracts a portion of the heat of the recently made soap, until the degree of that and its own is uniform. The foaming having subsided, the soap is racked off into the barrels, in which it is sent away. In the manufacture of soft soap, it is better that the boiling should be for too long a time than for too short. Soap which is not sufficiently cooked changes and spoils, while the only disadvantage produced by excessive boiling is a diminution in the quantity of the product. The usual time requisite for a charge is six or seven hours; but varies with the strength of the lyes, the temperature of the atmosphere, and other incidental circumstances.

In Great Britain a small proportion of tallow is usually introduced as one of the materials for the production of soft soap. This addition is for the purpose of producing the solid white granulations of stearate of potash, termed *figging*, because the soap then resembles the granular texture of a fig. Hence British soft soap presents the appearance of a brownish transparent body, through which white grains are disseminated. These figged granulations do not usually make their appearance until two or three weeks after the soap has been made, and during the hot summer months they do not appear at all. They are improperly considered to be a proof of the good quality of the soap, and hence the figged appearance is sometimes imitated by the admixture of starch.

The Scotch process for manufacturing soft soap is as follows:—273 gallons of whale or cod oil, and

400 lbs. of tallow are introduced into the soap-pan, together with 250 gallons of potash lye, of such strength that 1 gallon contains 6600 grains of real potash. Heat is now applied to the pan, and as the mixture approaches the boiling temperature, much froth appears, and to prevent boiling over it is beaten down on the surface. Should it subside quickly into a doughy-looking paste, it is an indication that too strong a lye has been used. Its proper appearance is that of a thin glue. There should now be added about 42 gallons of a stronger lye, equivalent to 8700 grains of potash per gallon, and after a short interval, an additional 42 gallons; and thus successively until nearly a total of 600 gallons has been introduced. After properly boiling, to complete the saponification of the fats, soap will be obtained amounting in quantity to 6400 lbs., from the above proportions of materials.

American soft soap differs very little from the preceding in its mode of manufacture; 200 lbs. of oil saponified by 72 lbs. of potash in lyes of specific gravity 1·110 = 22° Twaddell, yielding 450 lbs. of finished soap.

Fish-oil soft soap has usually a dark-brown colour, and that made from refuse fat and oil a dirty-white shade. Soap made with colza oil is slightly bluish. When hempseed oil is used, the soap has a greenish colour. The latter is by some consumers preferred to other kinds of soft soap; and hence ordinary soft soap made from fish oil is frequently tinged green by adding a small proportion of powdered indigo.

Soft soap is always of a pasty consistence, and even if excessively boiled, does not harden, but becomes scorched and dry. In this country it is chiefly used for fulling, and for the scouring and cleansing of woollen stuffs. Being possessed of greater solubility, and having a much more powerfully detergent action, it is also especially applicable for scouring floors and wooden utensils. In Germany, Belgium, and Holland it is also used for washing linen, which thereby acquires a most disagreeable odour of oil.

There are two qualities of soft soap in the market. They contain—

	1.	2.
Fat acids,	50·0	40·0
Potash,	11·5	9·5
Water,	38·5	50·5
	100·0	100·0

Soda Soft Soap.—In this soap part of the potash is replaced by soda. The product has the characteristics of soft soap, but contains more water.

The lyes must be free from salt, or obviously the product would be a hard soap; or if in too small a quantity for this, a certain quantity of hard soap would precipitate and render the soap turbid instead of transparent.

The best proportion is 1 part of soda to 4 of potash lye. A mixture of 100 lbs. of oleic acid (or red oil), 50 lbs. of tallow, and 3750 lbs. of hempseed oil, makes a good fatty mixture for this soap.

The *Savon vert* of Belgium and Germany contains about equal parts of potash and soda soaps.

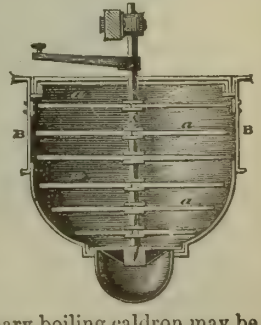
Hard Soap from Soft.—When chloride of sodium is added to soft or potash soap, decomposition ensues, the chlorine of the salt seizes the potassium of the soap, producing chloride of potassium; and at the same time the sodium takes the place of the potassium in the soap, and a hard or soda soap results. The proportions recommended by Pellétier and others for the conversion of soft into hard soaps, by means of the above-mentioned decomposition, are 6 lbs. of salt to every 3 lbs. of oil; and the solution of the salt in water is to be added in small portions and gradually to the soap, the latter being in a state of ebullition. The soda soap produced separates quickly from the lye, and the operation is terminated in the usual way. This process for producing hard soap is of great importance in those countries where soda is not to be procured, as potash and its salts may be substituted for the latter in the process of saponification.

Toilet Soaps.—*Scented Soaps, Little-pan Soaps.*—These soaps are ordinarily made without boiling, saponification being effected by mechanical means; or they are prepared by remelting and clarifying white or curd soap, and adding various perfumes, colours, &c. Most of these soaps are already described in the article Perfumery.

Cold Saponification.—The fat is melted at a low temperature, and filtered. A very strong lye is then gradually added (not less than 56° B.), and stirred well in with a wooden crutch, the mixture being heated, but not allowed to boil. When the stirrer draws a distinct ring, the colouring matter and perfume is added. The temperature must not be below 104° Fahr., nor above 149° Fahr. The paste should be united, homogeneous, and of some consistence. Pressed between the fingers, it should be unctuous, without being greasy. When it has reached this state, it is run into frames lined with linen, and closed in with a wooden cover, and left for twelve to twenty-four hours, when saponification will be complete. During saponification the temperature rises spontaneously to about 176° Fahr. When the soap is cool, it may be taken from the frames, cut, pressed, and dried; 112 lbs. of lard require 56 lbs. of caustic soda lye of 56° B.

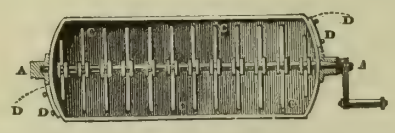
Hawes' Process.—The tallow or other fat is melted at as low a degree of heat as possible, and then mixed with the quantity of alkaline lye requisite to convert it into soap. The mixing is performed by mechanical means. Ordinary soap boilers' lye is used, preference being given to that made from the strongest and purest alkali. To each 100 lbs. of tallow are required about 20 gallons of lye made from strong alkali, and of specific gravity 1·125 = 25° Tw. An ordinary boiling caldron may be used as the combining vessel, with the addition of a

Fig. 8.



rotating fan to produce an intimate admixture and minute division of the tallow. Figs. 8 and 9 show the apparatus. An upright shaft, A, Fig. 8, which may be of wood or iron, and from which arms, *a a a a*, radiate to the sides of the caldron, is fixed permanently or temporarily in the copper. If more convenient, a cylinder (Fig. 9) may be employed,

Fig. 9.

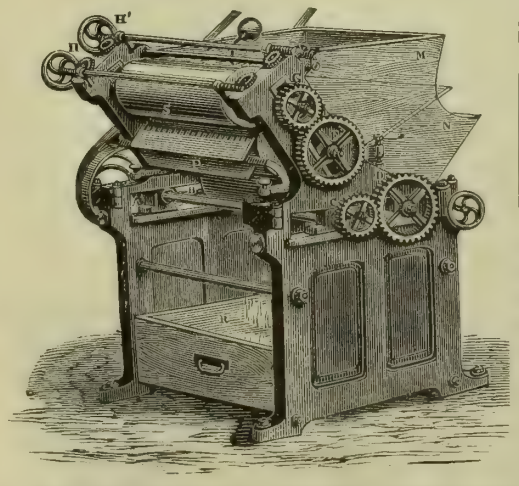


with a shaft, A, passing through it horizontally, and from which arms, *c c c c c c*, radiate, when a rotatory motion will thoroughly incorporate the fatty matter and the lye. For 2½ tons of tallow the cylinder should be about 6 feet in diameter and 12 feet in length. At DD are doors for filling and discharging the materials. The agitation must be continued for about three hours, or until the tallow is completely saponified, which is known by the mass becoming thick, after which it is allowed to stand from one to four days, according to the quantity of the paste. As soon as the mass thickens and the lye is absorbed, the cylinder should be emptied and the contents turned into an ordinary caldron, preparatory to being finished and converted into soap by any of the ordinary methods.

French Toilet Soaps.—The soap is cut into thin shavings by being pressed against a rotating wheel, having on its circumference a number of cutting blades.

The laminæ are then mixed with the requisite perfumes and colouring matters, and transferred to a mixing machine. Fig. 10 represents a mixer which

Fig. 10.



is much used in France. The soap cuttings, with the necessary ingredients to form the toilet soap, are placed in the hopper, N. Three pairs of cylinders, set in motion by the gearing, A B C D F G, the disposition of which is readily understood, crush the mixture into a paste. The distance of these crushing rollers is regulated by the screws, H H'. The mixture is carried upwards by the lower rollers, and passes through the upper series, S, which convey it into the hopper, M. This hopper when full is opened, and the paste falls into the lower hopper, N, whence it is again sent through the machine.

Soaps coloured with ochre, vermilion, or metallic oxides are passed five or six times through the machine; white soaps or dyed soaps two or three times only.

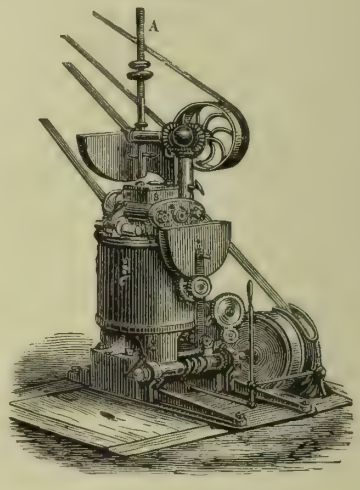
When the paste is perfectly homogeneous, a catch, which holds the plate, P, in position, is let go, and the mixture falls into the box, R.

The mass of moist soap is then weighed into lumps, and moulded, either by hand or by suitable presses, into the required shape, and placed in a drying chamber. When sufficiently hard, the cakes are stamped in moulds, and finally polished with a little alcohol to give them a good surface.

In the case of the best soaps the process of drying and moulding is repeated several times.

Fig. 11 is a moulding machine for cheap toilet soaps. The soap paste is placed in the cylinder, C; here it is pressed upon by a piston moved slowly downwards by the rod, A. At the bottom of the cylinder,

Fig. 11.



C, the soap passes into moulds, and is here submitted to the action of another piston, moving horizontally, which stamps the maker's name, and gives a polish to the surface. Round the cylinder, C, a current of steam circulates. to maintain the soap at the necessary degree of fluidity.

Analysis.—The proportion of water in mottled or marbled soap should never exceed 30 to 35 per cent. Properly prepared white soap should not contain more than from 40 to 45 per cent. of water. Frequently, however, the proportion amounts to 55 or 60 per cent., and cases have been known in which soaps combined with from 83 to 84 per cent. of water have been sold. This is either added directly to the soap when run into the frames, or the soap

is kept for some time in a solution of salt. The proportion of water is also sometimes increased by submitting the bars of soap to the action of high-pressure steam in tight chests or bins; also by boiling the soap in high-pressure coppers before *cleansing*.

The proportion of water contained in a sample of soap may be readily ascertained by treating a portion in a water or oil bath, until it ceases to lose in weight: 2 ozs. or more of the sample to be examined should be taken and reduced to small thin shavings. Of these, after carefully mixing together, 100 grains are taken, placed in a small porcelain or platinum crucible, and dried by exposure in a water bath for a sufficient length of time. When the weight remains constant, the operation is at an end. The difference between the first and last weighing indicates the percentage of water present.

To ascertain the amount of fatty matter, 100 grains of the soap are dissolved in 4 or 5 ozs. of boiling water, and the solution is filtered. A sufficient quantity of dilute acid is added to effect neutralization, and afterwards a weighed portion of pure and dry white wax. The whole is then heated until the wax is liquefied, and has combined with or taken up the oil or fat liberated from the soap by the stronger acids. After allowing it to cool the cake of wax obtained is removed and weighed; the increase above the original weight of the wax indicates the proportion of fat, oil, or grease contained in the soap.

If the fatty matter of the soap when liberated by the acid itself concretes on cooling, the addition of wax is unnecessary, as the fat may be weighed *per se*.

The liquid decanted from the fat, or solidified wax, may afterwards be submitted to examination, to ascertain the nature and state of purity of the alkali. If this is intended, hydrochloric acid should be used for the liberation of the fat. To ascertain the nature of the fatty material, Dumas directs the aqueous solution of the soap to be saturated with tartaric acid, the fatty acids to be collected, and their point of fusion carefully observed. It is a matter of great difficulty to determine the particular kind of fat or oil used in the production of the soap under examination; yet by the above method, it is possible at least to prove the identity of the fatty component; as, for instance, whether the soap is made from tallow or from oil, or whether it is of the same kind as the sample from which it may have been purchased. The odour evolved by the fatty acids at the moment of decomposition of the soap by a stronger acid, or that developed when the fatty matter so liberated is treated in a small porcelain dish, will often indicate the nature of the fatty substance employed in its production, or that at least which is present in the greatest proportion.

According to Normandy, another test as to the quality of the soap is, that the fatty or oily acid should be readily and completely dissolved by hot alcohol.

The estimation of the proportion of alkali contained in a sample of soap is frequently a point of great difficulty. When only one alkali is present, the determination is most easily effected by alkalimetry.

It not unfrequently happens that a soap contains more or less uncombined or non-saponified fatty matters; and in this case, when the soap is dissolved in water a film of oily matter is seen to float on the surface. The aqueous solution is decomposed by means of hydrochloric acid, when the fatty acids as well as the unaltered fatty matter collect together on the surface of the liquid. These are separated by filtration, thoroughly washed, and then treated with caustic baryta. The precipitate produced is thrown on a filter, washed with boiling water, and then acted upon by hot alcohol. By this means the non-saponified grease dissolved is from the soap of baryta; and after separation of the alcohol by evaporation, its weight may be ascertained. When tested by litmus paper, it should not show an acid reaction.

The following is a *resumé* of the method of analysis given by Richardson and Watts:—

The soap is dried over sulphuric acid, or in a water bath at 100° C., and is then dissolved in alcohol (100 grains require 3 ozs. of alcohol), and heated to boiling in a water bath. The soap, rosin, and free fat enter into solution, leaving the mineral constituents, glue, starch, dextrin, &c., undissolved. The liquid is filtered, and the residue washed with alcohol.

The alcohol is eliminated from the filtrate by the heat of a water bath. Addition of water then sets free any rosin or uncombined fat; these are collected on a filter, dried, and weighed.

The filtrate now contains only the fat soap and rosin soap, if any, and must be treated with a graduated solution of sulphuric acid, to determine the amount of potash or soda in combination with the fat acids. At the same time, the soap solution is decomposed; the fat and rosin acids rise to the surface, are collected on a weighed filter, washed with hot water, dried *in vacuo*, and weighed. The weight expresses the joint amount of fat and rosin acids in the soap. Cold alcohol will dissolve out all the fat acid, together with a small proportion of the rosin from the filter; and the filter, dried *in vacuo* and weighed as before, gives approximately the amount of rosin in the soap.

To determine whether the base of the soap is soda or potash, the solution of the sulphates filtered from the fat acids is concentrated, and treated with tartaric acid or dichloride of platinum in the usual way.

The filter containing the matter insoluble in alcohol is dried and weighed, after being thoroughly washed with alcohol. In genuine soap this insoluble matter is of very small amount, not exceeding 1 per cent. for mottled, and being even less for yellow soap.

Cailletet has proposed a method of analysis in which only one weighing is required. In soap 10 grams. in thin shavings is decomposed by a measured volume of sulphuric acid of known strength, in presence of a measured volume of oil of turpentine.

The fatty acids dissolve in the oil of turpentine and increase its volume; and this increase, multiplied by the specific gravity of the fat acid, determines its weight. The amount of alkali is determined by alkalimetry, and the water is estimated by difference.

The standard acid is prepared by mixing 189·84 grammes of the strongest sulphuric acid with sufficient distilled water to make up the volume to a litre at 15° C. Of this acid 10 c.c. neutralize 12·2 grammes of soda, and are therefore enough to decompose 10 grammes of soap.

Ten c.c. of the standard acid and 20 c.c. of oil of turpentine are poured into a tube containing 50 c.c., and divided into 100 parts; 10 grammes of the soap in thin shavings are then added, the tube is closed with a good cork, well shaken for a few minutes till the soap is dissolved, and then left at rest for a quarter of an hour till the oily solution of the fatty acids has completely separated from the watery liquid.

The volume of this oily solution is now to be read off, a deduction of half a division (·25 c.c.) being made to allow for the diminution of the capacity of the tube and consequent rise of the level of the oil, occasioned by the film of watery liquid adhering to the inner surface of the tube.

Bolley decomposes 1 gram. of soap in a small beaker with ether and acetic acid. Two layers of liquid are formed; the upper being an ethereal solution of the fatty acid and rosin, and the lower an aqueous solution of the alkaline acetate and of the salts contained in the soap; insoluble matters remain at the bottom as a residue. The liquids are separated by a pipette; the ethereal solution is evaporated in a tared glass over the water bath, and the residual fatty acid weighed. The watery liquid is evaporated to dryness in a platinum dish, ignited, and the alkali estimated in the usual way.

There are several other important considerations relating to the determination of the value of soaps. The problem to be solved by the soap boiler is the production of an article from which no more is dissolved or washed away, when it is employed as a detergent, than is absolutely necessary for cleansing purposes. When this is not the case, much soap is uselessly wasted. If the soap contains too much water, or its consistence be rendered too loose by reason of an excess of lye or salt disseminated through it, as is the case with many of the varieties of soap described, the waste from this cause will be proportionately great. On the contrary, if the soap is over dry, much laborious exertions will be required to detach a sufficient quantity for the purposes required. Curd soap is the only kind which maintains the proper mean between these two opposing characters, and this is due to the quantity of water which it contains, and its state of solidity. Soap that has become too dry is improved by being kept in a moist place, and an opposite treatment improves soap that contains too much water. But, of course, as regards the foreign salts they contain, no alteration or improvement can take place. Curd soap is therefore the proper form in which soap should be sold; no deception need, however, be practised, when soap contains a large amount of water, as, for instance, cocoa-nut oil soap, provided a corresponding reduction be made in the price. The same remark applies to soap prepared from bones, fuller's earth, silica, &c., which, if they cannot positively be called adulterations, are very much calculated, like the former, to promote dishonest traffic. The production of these articles will find very little encouragement when the soap boilers understand their own interests and responsibilities. These remarks, of course, do not apply to soft soaps, which are used for entirely different purposes.

In the appended table the great discrepancies in the value of different kinds of soap are pointed out.

Variety of Soap.	Fatty Acids.	K_2O.	Na_2O.	Water.	Analyst.
Castile soap, specific gravity 1·0705,	76·5	"	9·0	14·5	Ure.
Castile soap, specific gravity 0·9669,	75·2	"	10·5	14·3	"
Fine white toilet soap	75·0	"	9·0	16·0	"
Ordinary white soap from Glasgow,	60·0	"	6·4	33·6	"
Mottled tallow soap of good quality, prepared from potash after having been kept for several years,	81·25	1·77	8·55	8·43	Heeren.
Brown rosin soap from Glasgow,	70·0	"	6·5	23·5	Ure.
London cocoa-nut oil soap—marine soap,	22·0	"	4·5	73·5	"
Hard poppy oil soap,	76·0	"	7·0	17·0	"
French white soap,	50·2	"	4·6	45·2	Thénard.
Marseilles marbled soap,	64·0	"	6·0	30·0	D'Arcet.
" "	60·0	"	6·0	34·0	"
White Marseilles soap,	68·4	"	10·24	21·36	Braconnot.
White Leipzig tallow soap,	76·3	8·8		14·7	Abendroth.
" "	50·0	9·4		29·8	"
Leipzig marbled soap,	45·0	9·8		38·0	"
Soft soap,	44·0	9·5	"	46·5	Thénard.
London soft soap,	45·0	8·5	"	46·5	Ure.
Belgian soft or green soap,	36·0	7·0	"	57·0	"
Scotch soft soap,	47·0	8·0	"	45·0	"
Good green soap,	34·0	9·0	"	57·0	"
Scotch soft rape oil soap,	51·6	10·0	"	38·33	"
Scotch soft olive oil soap,	48·0	10·0	"	42·0	"
Semi-hard soap for fulling,	62·0	11·5	"	26·5	Verviers.
Ordinary soft soap, 1st sample,	44·0	9·5	"	46·5	Chevreul.
" " 2nd sample,	42·8	9·1	"	48·0	"
" " 3rd sample,	39·2	9·8	"	52·0	"

SODA.—SODIUM CARBONATE; SODA ASH; *Soude, Carbonate de Soude, Soude Carbonatée*, French; *Soda, Kohlensaure Natron*, German. Symbol, Na_2CO_3.

This salt exists in the soda lakes of Egypt and Hungary, and in many mineral waters, though not in sufficient quantity to pay for its extraction. In France, Spain, and other countries where common salt is scarce, or where the duty on it is so high as to prevent its economic conversion into carbonate of soda, plants are extensively consumed for the soda they contain. In some places native carbonate of soda is found, being the residue of the evaporation of mineral waters.

Soda was formerly procured almost entirely from marine plants. These contain soda (according to DUMAS, as oxalate), and this by calcination is converted into sodium carbonate. The plants were dried in the air, and then burnt in rude furnaces, at a temperature just sufficient to cause the ashes to fuse together into compact cellular masses. The substance thus obtained was known by various names, according to the country whence it was procured and the kind of plant consumed. Among these were the "barilla" of Spain, "kelp" of Scotland, "varec" of Normandy and Brittany, &c.

The soluble portion of these ashes consists of sodium carbonate, sulphate, thiosulphate, sulphide, iodide, bromide, chloride, ferrocyanide, and to a small extent the corresponding potassium salts. The insoluble matters are calcium phosphate, carbonate, and sulphate, magnesia, silica, alumina, ferric sulphide, and carbon.

Of the several varieties, *barilla* is by far the most valuable. It contains from 14 to 20 per cent. of sodium carbonate. It has a greyish-blue colour; and when exposed to the air for some time effloresces at the surface. It is difficult to pulverize, and has a pungent alkaline taste. The plant yielding barilla is the *Salsola soda;* it is carefully cultivated on the coasts of Spain for the purpose of this manufacture. The following table shows the composition of various kinds of ash:—

Constituents.	Alicante.	Cherbourg.	Cherbourg.	Unknown.	Unknown.	Spain.	Villette.	Granville.
Potassium sulphate,	—	22·19	42·54	18·80	22·00	15·85	20·35	13·50
Potassium chloride,	—	16·00	19·64	—	—	10·55	10·53	15·60
Sodium chloride,	65·00	45·78	25·38	73·20	68·00	68·35	54·11	65·68
Sodium carbonate,	2·00	9·53	3·71	6·00	6·00	traces.	13·76	·22
Calcium sulphate,	—	—	—	—	—	1·10	—	—
Insoluble matters,	3·00	1·50	·73	—	—	—	—	—
Iodine compounds,	—	traces.	traces.	traces.	traces.	—	traces.	traces.
Sodium sulphate,	30·00	—	—	—	—	—	—	—
Water,	—	5·00	8·00	2·00	4·00	4·00	1·25	5·00
Loss,	—	—	—	—	—	·15	—	—
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Kelp is the residue of various species of *fuci*. Two specimens gave the following results:—

	Helsker.	Rona.
Sodium sulphate,	8·0	19·0
Sodium carbonate and sulphide,	8·5	5·5
Sodium and potassium chlorides,	36·5	37·5
	53·0	62·0
Calcium carbonate,	24·0	10·0
Silica,	8·0	—
Alumina, with a little ferric oxide,	9·0	10·0
Calcium sulphate,	—	9·5
Sulphur and loss,	6·0	8·5
	100·0	100·0

Sea weeds from the mouth of the Clyde yield—

	Fucus Digitatus.	Fucus Nodosus.	Fucus Serratus.
Potash,	22·40	10·07	4·51
Soda,	8·29	15·80	21·15
Lime,	8·79	10·98	11·09
Magnesia,	7·44	10·93	11·66
Sodium chloride,	28·39	20·16	18·76
Sodium iodide,	3·62	0·54	1·33
Calcium phosphate,	5·63	3·34	9·67
Ferric oxide,	0·62	0·29	0·34
Sulphuric acid,	13·26	26·69	21·06
Silica,	1·56	1·20	0·43
	100·00	100·00	100·00
Percentage of ash in weed dried at 100° C.,	20·40	16·19	15·63

The most valuable of the French ashes is that known as *salicor* or *Narbonne soda*, which is the residue of the combustion of the *Salicornia annua*. It contains from 14 to 15 per cent. of the alkaline carbonate. Another kind, also valuable, is *blanquette* or *Aiguemorte soda*, extracted from the *Salicornia europæa*, the *Salsola tragus*, the *Atriplex portulacoides*, the *Salsola kali*, and the *Statice limoneum*. The first-named of these yields the most soda, and all contain abundance of common salt. The amount of carbonate of soda in *blanquette* varies from 3 to 8 per cent. *Varec* is the ash of plants belonging to the species *fuci*. This is the least valuable of the French native sodas; but it contains much sulphate of soda and potash, chloride of sodium and potassium, and a little iodide of sodium. It is principally extracted for the sake of its potassium salts, and is used in the manufacture of saltpetre. It is also valuable as a source of iodine. The commercial demands for soda are now supplied almost exclusively by an artificial method of production. Barilla and kelp are used to a small extent in the soap manufacture as a substitute for chloride of sodium, and in Scotland sea weeds are still consumed as a source of potash and of iodine (see IODINE and POTASSIUM).

HISTORY.—Soda ash is now manufactured from sodium chloride on an immense scale. It has already been mentioned that *barilla* is by far the most valu-

able native ash. On the coasts of Spain this ash was formerly produced so abundantly as to supply, not only the native demand for soda, but also that of other countries.

Great Britain produced large quantities of native soda under the form of *kelp*, the manufacture of which was carried on at a very early period on the North and West coasts of Ireland, and later on the Western shores and islands of Scotland. This trade was especially brisk at the commencement of the present century, when, to meet the exigencies of the war, high duties were imposed upon the Spanish barilla. The annual rental of the kelp shores of the island of North Uist alone amounted at this time to £7000; and at one period the entire quantity of *kelp* produced in Scotland and its adjacent islands was estimated at more than 25,000 tons annually. Still, even this quantity of native soda was not sufficient to supply the national needs.

France was especially dependent on Spain for soda; and when at the time of the French revolution of 1789 the importation of barilla was suspended, the National Convention made, in a special proclamation, an appeal to the chemists of France to devise a process by which common salt might be rendered available as a source of soda. To the appeal of the Convention due response was made, and numerous plans were proposed; but of all the processes communicated to the committee intrusted with the examination and execution of the various proposals, the only one deemed likely to be successful was that of Leblanc. The first establishment for prosecuting the manufacture on a large scale was erected in 1804 at St. Denis by Leblanc, and was carried out by him and his partners, Dizè and Shée. Leblanc, after having spent all his means in perfecting his plan, was neglected by the government of his own country, and though handsomely rewarded by the British government, at last died in an hospital. In Greece and at Rome statues have since been erected to his memory.

The principle of this process was foreshadowed in England by Dr. Brian Higgins *as early as* 1781. His paper shows that he started with common salt, which he decomposed into sulphate of soda and hydrochloric acid by oil of vitroil. The dry sulphate or salt cake obtained was put into a reverberatory furnace, with one-eighth of its weight of coal, and heated till the ingredients were melted, and the sulphate reduced to the state of sulphide. At this stage twice its weight of lead was introduced, and when the metal was melted, the whole was stirred with an iron rod until the sulphur united with the lead, and the fused caustic soda floated in a distinct layer over the surface of the sulphide of lead. The furnace was then tapped to allow the alkali to flow out.

The great expense attending this plan, arising from the high price of lead, rendered it valueless as a commercial process; but in the same patent Higgins states *that iron introduced into the furnace, or other metallic oxides, may be used equally well.* Here, therefore, is clearly developed the principle of Leblanc's process. Leblanc, however, had the sagacity to replace the expensive oxide of iron by oxide of calcium, and the process practised in Great Britain at the present day is substantially that devised by him.

The first step in the manufacture is the production of salt cake (sodium sulphate) by the action of oil of vitriol on common salt.

Sodium Sulphate. — Glauber's Salt, Salt-cake; *Sulfate de Soude*, French; *Schwefelsaures Natron*, German. Symbol, Na_2SO_4. This compound of sodium was discovered by Glauber in 1658. It is found copiously in nature as a constituent of mineral waters, and to a small extent in the mineral form as mirabilite.

Sulphate of soda in the form of mirabilite is found in Austria, in Bohemia, in the Tyrol, and in several places in Spain and Hungary, as well as in Switzerland; on lavas, and as an efflorescence on the Siberian and Caspian steppes. A mixture of the crystallized salt with gypsum—*Glauberite*—was discovered by Gimbernat in the canton of Argovie in Switzerland; the same compound has been found in crystals and reniform masses, embedded in rock-salt, at Villarubia in Spain, at Vic in Lorraine, Berchtolsgaden in Bavaria, and at Atacama in Chili.

Sodium sulphate is a by-product in the preparation of nitric acid, of sal ammoniac, of carbonate of magnesia, in the amalgamation of silver ores; and it may also be obtained from many glass slags, if native or artificial soda has been used in the preparation of the glass.

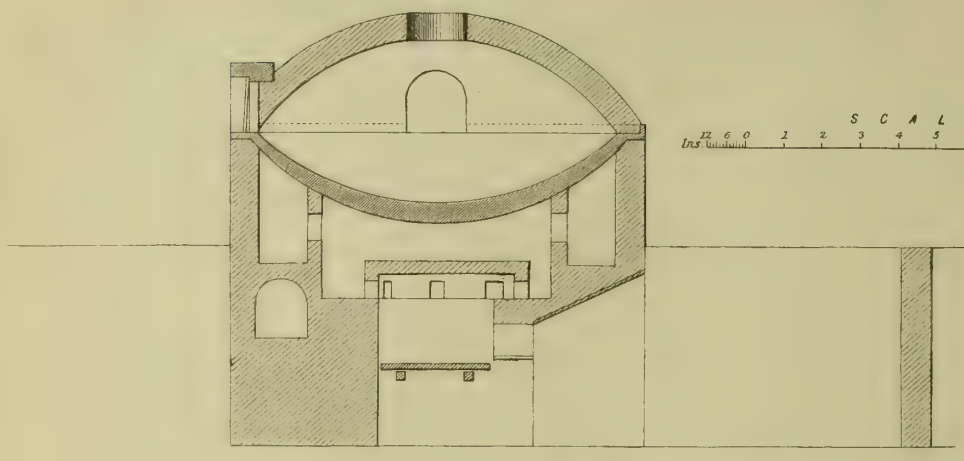
Pure sodium sulphate is prepared by addition of sulphuric acid to sodium chloride; hydrochloric acid is set free and sodium sulphate produced. When effervescence has partially subsided heat is applied, and continued till the whole of the hydrochloric acid is expelled.

The dry mass usually contains a little sulphuric acid; this is removed, after solution in water, by the addition of a sufficient quantity of carbonate of lime, or the excess of acid may be neutralized by the addition of carbonate of soda. The solution is then filtered, evaporated, and set aside to crystallize.

Crystals of sodium sulphate have the composition $Na_2SO_4 + 10H_2O$; their form is the oblique rhombic prism. The anhydrous salt is obtained by heating the hydrated sulphate to redness or, according to Faraday, by evaporating an aqueous solution at a temperature considerably below 100° C. The crystals belong to the right prismatic system. This latter, which is transparent, when exposed to the air becomes opaque on the surface, owing to absorption of water. The taste of the crystallized salt is cooling and bitterish saline. By exposure to the air it effloresces, with the loss of all its water. The perfectly effloresced salt intumesces in very moist air to three times its bulk, and then becomes a crystalline mass of ordinary Glauber's salt, with a slight excess of water. When the crystallized salt is heated, it fuses, gives off its water, and thereby becomes a white solid; but at a red heat this again becomes liquid: 1 part of the crystals dissolves in 3 parts of water

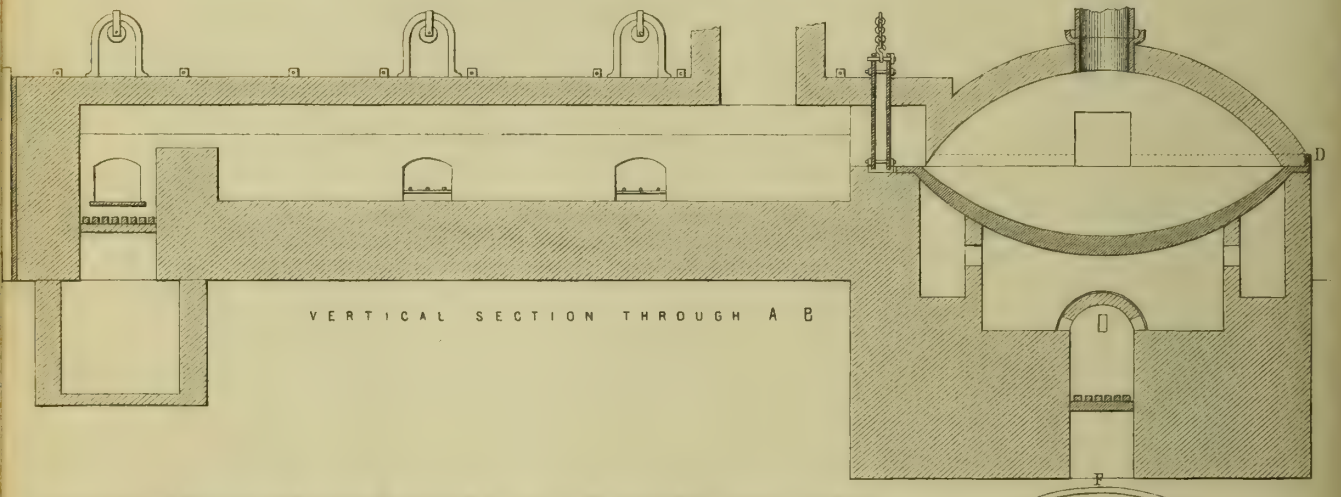
S O D A.

DECOMPOSING FURNACE & PAN (OPEN DRIER.)

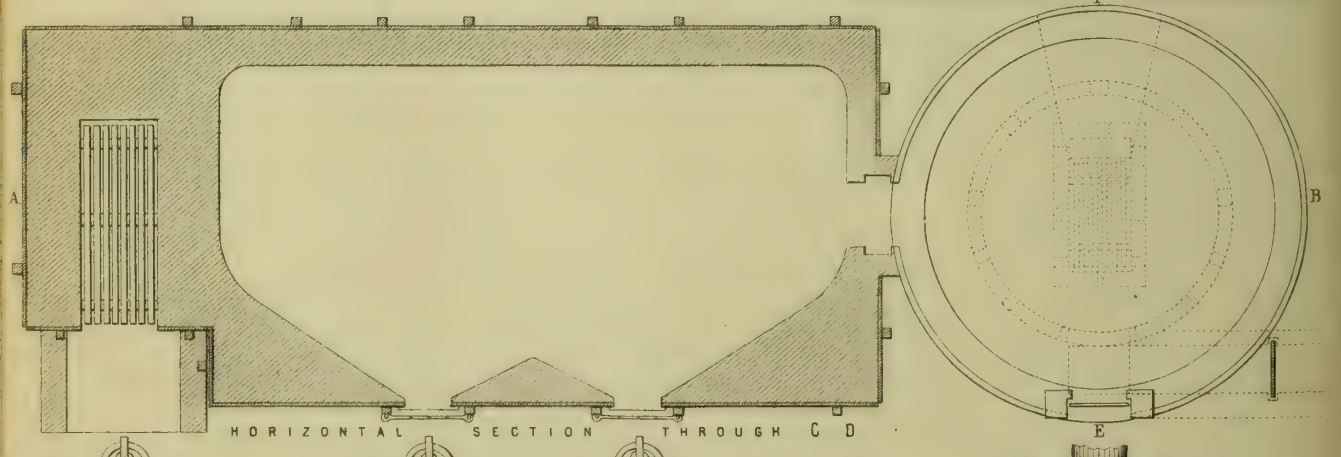


SCALE
Ins. 12 6 0 1 2 3 4 5 6 7 8 9 10 Feet

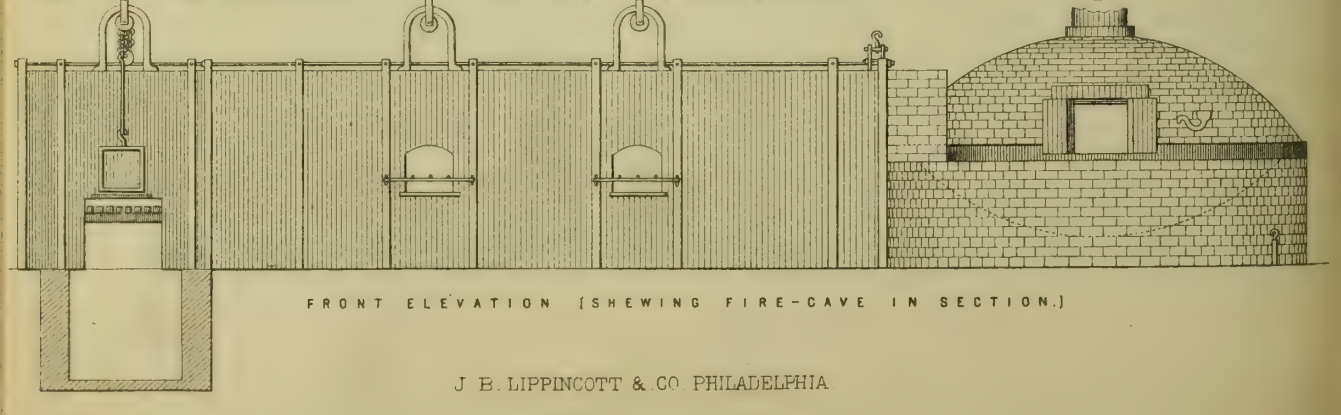
VERTICAL SECTION OF PAN THROUGH E F



VERTICAL SECTION THROUGH A B



HORIZONTAL SECTION THROUGH C D



FRONT ELEVATION (SHEWING FIRE-CAVE IN SECTION.)

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at 15° C.; at 100° C. water dissolves its own weight of the salt. It is insoluble in alcohol. A crystallized sulphate of soda is also known, containing 8 equivalents of water, and having the formula $Na_2SO_4 8H_2O$.

Sulphate of soda is a mild but efficient cooling laxative or purgative salt. It was formerly the most favourite saline cathartic in this and other European countries, but since the beginning of the present century has gradually been displaced by the sulphate of magnesia.

Manufacture of Commercial Sulphate of Soda (Salt-cake).—By far the largest quantity of this article is manufactured for the purpose of serving as a material in the manufacture of soda ash; and this is nearly always done in the alkali works themselves, one of whose principal branches it forms. Only exceptionally sulphate of soda is made as a by-product from the manufacture of muriatic acid, the relation between them in alkali works being always the other way; in the former instance it is made in cylindrical cast-iron retorts, very similar to those used for nitric-acid making, and the acid is condensed in a series of stoneware Woolfe's bottles. This product is known as "cylinder cake," and frequently contains a good deal of undecomposed salt. On the other hand, in some cases, but rarely in this country, sulphate of soda is made purposely for glass making; and as in this case (except for common glass) it must be as free from iron as possible, it is made in leaden pans. The great bulk of sulphate of soda is made in the large cast-iron pans or pots first introduced by Gamble or Lee (it is not quite certain by which of these in the first instance), or by the recently introduced process of Hargreaves and Robinson, which will be afterwards described; but it is very probable that the mechanical furnace introduced by William Jones, of Middlesborough, which will be described below, will cause an important revolution in this manufacture.

The raw materials for sulphate of soda making are sulphuric acid and common salt (sodium chloride). Both of these are treated of in their respective places; and it need only be mentioned here, that the sulphuric acid need not be pure, nor any more concentrated than as it is furnished by Glover's towers, or even by the first acid chamber; it is only when sulphate nearly free from iron (for glass-making) is required, that attention has to be paid to this point in the acid. The common salt used in this country is always that from Cheshire, which is not only cheap, but also remarkably pure. The salt used abroad often contains very many impurities (especially calcium sulphate), which greatly injure the quality of the salt-cake, and subsequently that of the soda ash made from it.

These two materials, in acting upon each other, ultimately produce the following result:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

This decomposition does not take place quite smoothly and all at once, but gradually, since the sulphuric acid always inclines to form acid salts (hydrosulphates). For this reason the hydrochloric acid is only partially driven off at a moderate temperature, and the remainder requires a very much higher temperature for its elimination. The first stage (at a moderate heat) takes place thus—

$$2NaCl + H_2SO_4 = NaHSO_4 + HCl + NaCl.$$

The second stage (at a stronger heat)—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The second stage, however, always partly sets in during the first period. Anyway there are always (except in Jones' machine) two stages in the manufacturing operation as well—viz., first, moderate heating in a metal vessel (pan); and secondly, strong heating (ignition) in a furnace. The hydrochloric acid evolved in the first stage, from the pans, is both more concentrated and pure than that from the second stage, the furnacing, where a little sulphuric acid always accompanies the escaping gases.

The usual process of salt-cake making in decomposing pans is always carried out in these two successive stages—viz., first, in the pan itself, where the decomposition is not carried right through; and secondly, in the furnace ("roaster" or "drier"), where it is completed. The process in the pans themselves is essentially the same everywhere, although there are not unimportant modifications in detail in the shape and in the mode of setting and firing the pans. But a much larger difference exists in the furnaces, which may be either "close roasters"—that is, muffle furnaces, where the flame does not come into direct contact with the batch; or "open furnaces"—that is, reverberatory furnaces, where the flame plays direct upon the batch. The former construction is more usual in Lancashire, Scotland, &c.; the latter is the only one found on the Tyne. Each kind of furnace has its advantages and its disadvantages, as will be seen hereafter. A third kind, where the flame first travels underneath the bed, and then directly over the charge, has been tried with gaseous fuel, but does not seem to have met with much approval.

Decomposing Pan.—This vessel is cast of particularly tough metal (the mixture of different brands most suitable for this purpose is considered a trade secret by the comparatively few iron-founders who cast these pans), forming a segment of a globe, as seen from the diagrams. They are usually from 2 to 3 inches thick near the top and from 5 to 7 inches thick in the centre; but a few manufacturers prefer to have them made thickest about half-way up. The weight of a pan, of about $9\frac{1}{2}$ feet diameter and 2 feet depth, is about 6 tons. In the majority of cases their upper margin is either plain or provided with a horizontal flange, and in this case they are covered over by an arch, which leaves the sides of the pan quite clear, and allows it to be withdrawn and replaced without disturbing the brickwork. This is a certain advantage, though more in time than in money; but for all this the construction shown in Plate I. is preferable, where the pan is provided with an upstanding rim in addition to the flange, and the covering arch is sprung from this rim itself in the

form of a cupola of half a brick's thickness. In the latter case it is impossible that the arch should be damaged by the boiling over in the pan without its being noticed, and in no case is it possible that any gaseous hydrochloric acid can find its way unperceived into the fire flues, and thus escape reaching the condensers. To be sure, the arch must be renewed every time a new pan has to be put in; but this can be done in a few hours' time, during which time the furnace may be heating up again. Plate I. also shows an excellent way of arranging the fire underneath the pan, about which there are many opinions. Very much depends upon this arrangement, both for the amount of work to be got out of the pan, and for the time it will last. The setting as shown will allow of the greatest possible production of salt cake by the pan, without preventing it from being worked at a slower rate, if necessary.

Sometimes the decomposing pan is heated by the waste heat from the muffle furnace; but this arrangement is quite erroneous when anything like a large and regular production is required. In a few cases, again, the fire is carried, not only under, but also over the decomposing pan. If divided from it by an arch, it is intended to prevent a condensation of hydrochloric acid, which, however, in any case does not take place in or near the pan. If the fire is directed over the pan itself, as is done in a few cases by means of the flame of an adjoining "open drier," it hastens the work, but dilutes the acid gas so much that the condensers do not yield anything but weak acid. Neither arrangement is adopted in any large number of works.

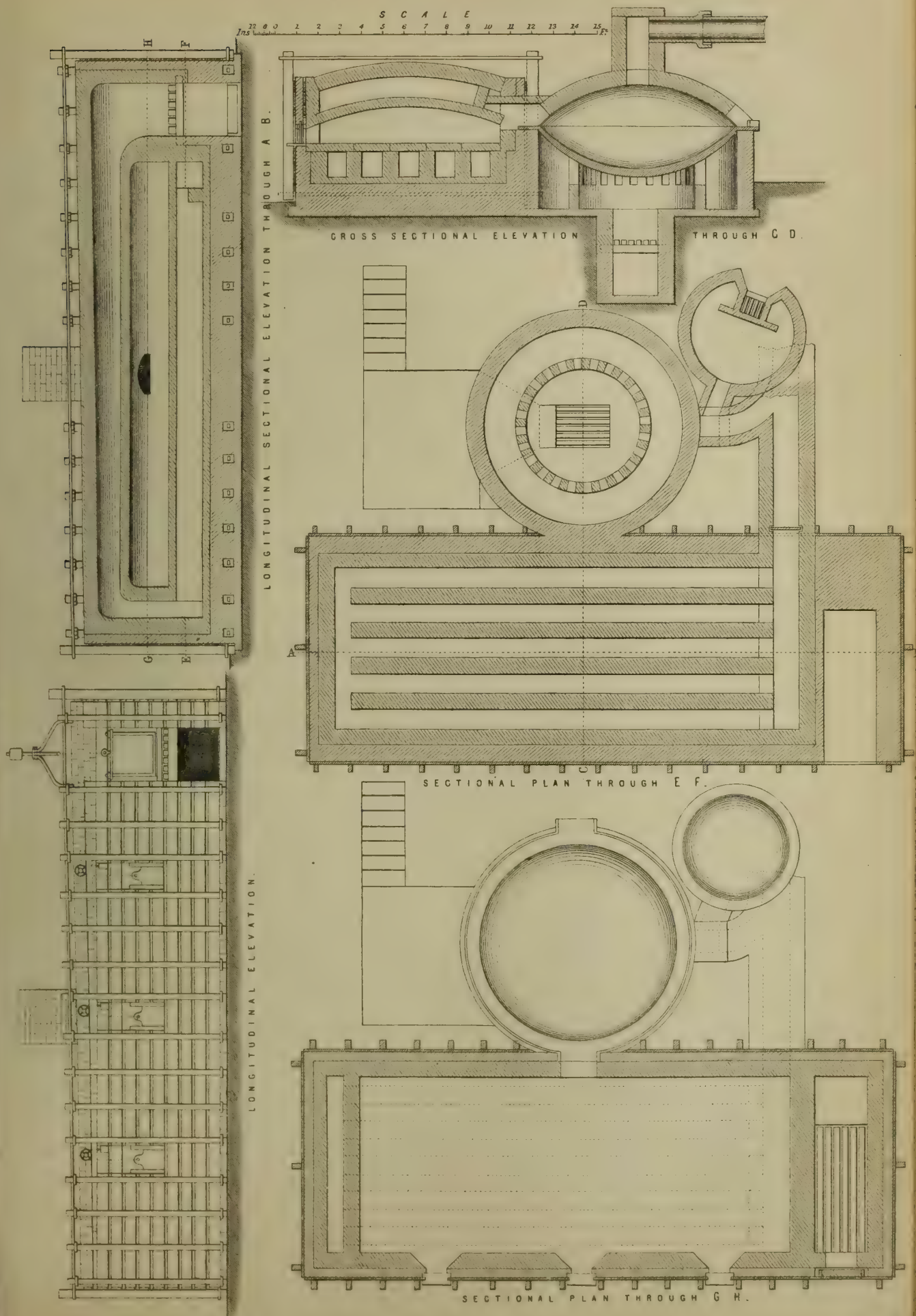
In every case there is a working or charging hole provided in front of the pan, generally shut during the operations by a leaden door, with a round opening for the handle of a rake to pass through; through this door the salt is thrown in and the charge worked. Another opening leads out of the pan into the furnace, known as the "shoving hole" or the "gangway." This is either opposite the charging door, in which case the charge is pushed through by means of a rake, and the pan then forms a continuation of the length of the furnace; this is called "shoving." Or the second opening is placed at right angles to the charging door; the pan is then called a "casting" pan, and the charge is removed by means of a large shovel ("casting shovel") with a long iron handle, worked through the charging door. In this case the pan is fixed at one side of the furnace. Local convenience must decide which arrangement is to be preferred; the engravings show the former. In any case the shoving hole is provided with a cast-iron damper, which is only lifted during the time of shoving or casting; and as these dampers are soon acted upon by the acid and do not then shut tight, it is a great improvement to use a double damper — one modification of which is shown in Plate I. — the space between the dampers being filled with salt. Salt is also heaped round the top of the damper, and in front of the working door, to keep the gas in. Each pan has further an exit pipe for the hydrochloric acid gas, from 12 to 18 inches in diameter; these pipes rise perpendicularly to such a height that from thence there is a continuous fall towards the first condensing cistern, or towards the condenser itself, if there are no such cisterns provided. The pipes are made of very carefully-prepared fire clay and are well boiled in tar; latterly they have been also made of glass. Lastly, there is beside each pan a gauging cistern for the sulphuric acid. This is usually of cast iron lined with lead, is heated from underneath by the waste heat of the pan flue, or otherwise, and is provided with a gauge float or other means of accurately measuring the acid; and with a self-acting syphon, which discharges itself into a cast-iron pipe leading through the pan arch into its interior, not quite on its margin, but a little way in, so that the acid runs on to the salt, not on to the metal, which would very soon wear away in this place. These cast-iron pipes wear out very soon, and must be replaced from time to time.

The calcining furnace itself, as mentioned above, may be either an "open drier" or a "close roaster." An excellent form of open drier, such as used on the Tyne, is shown in the diagrams on Plate I., which render any further explanation almost superfluous. The fire-places, the connection with the pan, the working-doors, which likewise serve for discharging ("drawing") the sulphate, the escape flue for the gas, &c., are clearly visible. These furnaces go a long time without any essential repairs, provided that they are lined with very hard, well-burned fire-bricks, capable of resisting the acid, which is of far greater importance in this case than mere resistance against heat. The whole arrangement shown on the plate (pan and drier together) represents essentially the plans used in all Tyneside works, although of course there are differences in unimportant details in every factory.

The "close roaster" is shown in Plate II.; the arrangements of the pans and flues explain themselves. These furnaces are subject to more repairs than open driers; they must be built with extraordinary care to begin with, since otherwise the acid gas soon finds its way through cracks in the arch and in the beds, and what is almost worse, the melted sulphate itself runs through any chinks in the bed and stops up the flues underneath. Such cracks are often only discovered after the gas has escaped through them into the fire-flue for some considerable time; and in the opinion of the Tyneside ash makers it is far more difficult to insure a complete condensation of the muriatic acid when using close roasters than with open driers, where such escapes are impossible, as the acid gas goes into the condensers at the same time with the fire gas. The great advantage of close roasters is the greater concentration of the acid gas, which certainly not only allows it to be condensed *more easily*, that is, with smaller condensers, but also to make more highly concentrated muriatic acid from them; and formerly it was assumed that this would insure a *more complete* condensation than with open roasters, but the above-mentioned difficulty of keeping the real muffle

S O D A.

DECOMPOSING FURNACE & PAN (BLIND ROASTER.)



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part of the furnace tight, practically turns the scale the other way, since those who use open roasters have learned to attain equally complete condensation by employing long cooling shafts or pipes (preferably of cast iron) and condensers of large size. Still they cannot get their condensed acid as strong as that from close roasters, and if they use coal for firing, the acid is too weak for anything but bicarbonate making; though by using coke as fuel it can be obtained about 18 to 20° Tw. (especially by using stone cisterns for a preliminary condensation, in which the gas meets the acid flowing from the condensers), and by mixing with the acid from the pan-condensers a sufficiently strong acid for chlorine making is obtained. The safety in respect to the escape of acid gas is not the only reason in favour of open driers; they certainly yield a considerably higher output and stronger sulphate than close roasters on account of the greater heat, and their wear and tear is very much less. Where it is not of importance to obtain practically the whole of the muriatic acid in a strong form, open driers seem to deserve the preference.

Fig. 1.

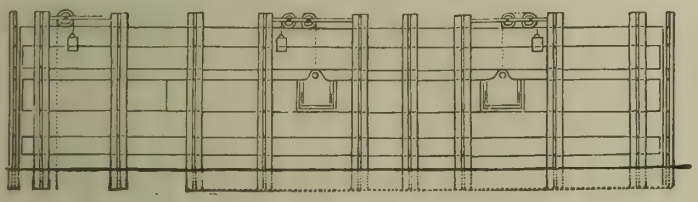


Fig. 2.

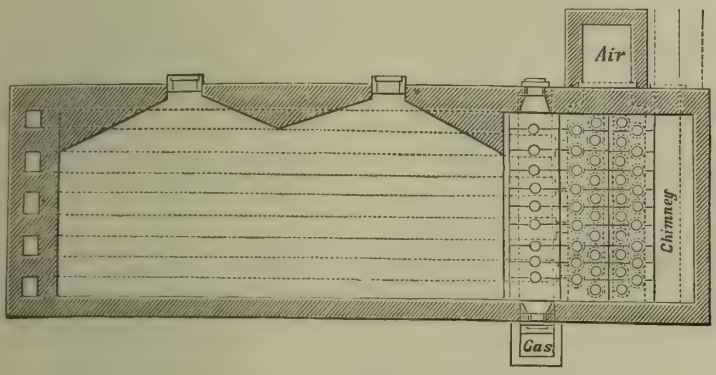


Fig. 3.

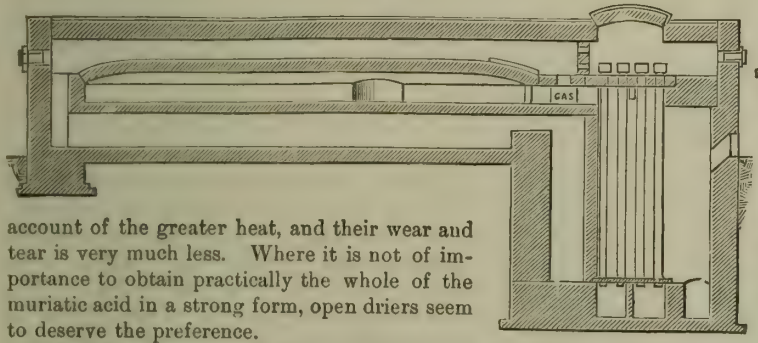


Fig. 4.

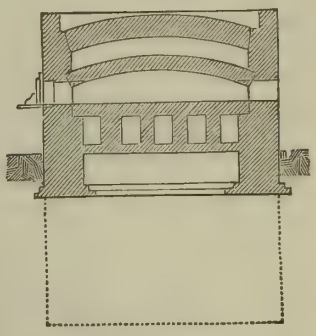
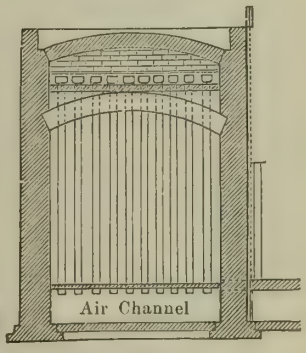


Fig. 5.



It has been mentioned above that Siemens' gas generator has been proposed for heating decomposing furnaces, and furnaces thus constructed have been worked for some years at Runcorn. In these the gas is inflamed in front of the furnace and first travels underneath its bed, and then returns over the same, but is not separated from the charge by an arch. Thus the risk of any gas escaping into the fire-flue is avoided, and it was assumed that it would be possible to burn the gas with a smokeless flame, and condense the acid from it as easily as from close roasters. This is, however, not the case, and the drawback of sulphate fluxing through the bed into the flues exists in full force. More fuel and labour is required for this plan than for direct firing, and it has not made its way among the trade to any extent. Quite lately another style of gas furnace has been made known, constructed by Gamble. It is a real close roaster, fired by gas instead of by an ordinary coal fire. The air is heated before being admitted to the gas, and a certain pressure is maintained in the gas generator, so that no acid gas from the interior of the muffle can escape outside. If this plan is carried out with sufficient care it will no doubt work well; but only in that case. This furnace is shown in Figs. 1 to 5.

An arrangement found frequently in Belgium is this—that the discharging of the furnace takes place through openings in the bed in front of the working doors, an arch being built underneath to receive the sulphate; the gas evolved during its cooling thus goes through the furnace and into the condenser.

This arrangement entails more labour in discharging a furnace, as each batch has to be lifted twice; but it prevents to a certain extent the nuisance of the gas arising from freshly drawn sulphate.

The work in the pan or furnace is as follows:—Supposing the pan has just been heated up, or else the previous charge has just been "shoved," the salt belonging to the new charge is shovelled in as quickly as possible through the charging door; and when about half of it is in, the acid syphon is let down so that the sulphuric acid begins to run in as well. The quantity of salt for one charge varies very much. In working with open driers it is almost universally the custom to work one batch each hour—these batches varying from 6 cwts. of salt up to 10 cwts. With close roasters the charges are mostly larger, being from 12 to 15 or even 18 cwts. of salt; but then only from 8 to 12 batches are made in twenty-four hours. In any case the quantity of sulphuric acid must be exactly measured, though the bulk of acid for a certain quantity of salt will, of course, vary very much according to the strength of the acid and to its temperature. As far as the strength is concerned, the stronger the acid is, the better, up to 144° Tw.—a strength which is frequently reached at the present time when Glover's towers allow of the concentration of all the acid made in most alkali works. On the other hand, where there is no convenience for concentrating the acid, it is sometimes used as low as 120° Tw.; but the weaker the acid, the more time and coal does it take to do the work, the more difficult is the condensation, owing to the large amount of steam, and the more quickly are the pans worn out. As, however, in no case does the acid run with exactly equal strength, its specific gravity must constantly be tested with the hydrometer, and more or less run into the pan according to its indications.

If the acid comes hot enough from the towers or pans, it is not necessary to heat it in the gauge cistern; but if cold, the latter ought to be heated so that the temperature of the acid may at least reach 120° Fahr., otherwise it cools the pan (which is already greatly cooled by the salt) far too much, and may even cause it to crack. The absolute quantity of the acid to be used depends very much upon the quality of the sulphate desired; if strong sulphate has to be made, as is usual in open driers, the proportion of acid of 144° Tw. to Cheshire salt of average moisture will be about as 95 : 100. When the salt is either drier or wetter than usual, a corresponding allowance of acid must be made. The result of the testing of the furnaced sulphate of soda furnishes, however, a daily control whether the proper quantity of sulphuric acid has been used or not.

When all the acid has been run in, and all the salt is charged, the whole is well mixed by means of a light iron rake. At this stage the mass is very liable to froth and even to boil over, which very soon destroys the pan arch; and it is therefore usual to throw a few ounces of tallow or other grease into the pan, in order to keep down the froth. The door is then put on and made tight with salt, but the rake is left in and occasionally worked about; the salt serving as a kind of stuffing box for the gas. After about half an hour the salt will be dissolved in the acid (for large batches it takes more time); the open coarsely-crystallized form of the Cheshire "common salt" greatly facilitates the dissolving, whilst the finely-crystallized "butter salt" of Cheshire, or finely-ground rock-salt, are much more difficult to treat, because they do not allow the acid to penetrate very easily through their whole mass. Rock-salt must be somewhat coarsely ground. After the salt is all dissolved, the fire is urged more strongly, in order to "boil down" the batch, and this is continued until the mass becomes so stiff that the workman feels considerable resistance to the working of the rake in it. He then slackens the fire, pulls up the damper, and removes his charge into the furnace, which by that time must have been emptied of its own charge. The removal is effected, in case of "shoving," by means of an iron rake whose head is bent in a slight curve, and follows the sweep of the pan; in case of "casting," by means of a large, slightly hollowed shovel with iron handle. The gangway is a little higher than the furnace beds, which facilitates the pushing over. The pan is then at once charged as before. In one work a second charge is put in the pan before the first is removed, and only half is shoved over; this is said to save the pans greatly from breakage, as they never go empty.

In the furnace the batch is at once spread out in an even, thin layer, and exposed to the heat of the fire. During the operation it is several times turned over by means of a "paddle," similar to the ball furnace paddles to be described afterwards; the lumps are crushed down, and the whole is now and then raked through with a tooth-rake. Great care is requisite to mix up all parts of the batch, otherwise there will be portions of it very poor, that is, containing undecomposed sodium chloride; and others over strong, containing sodium bisulphate. It is evident that this careful working is very much easier in a reverberatory furnace, both because it is lighted up by the fire, and because the heat is so much greater than in a muffle furnace, which is at first quite dark, and only towards the end of the operation becomes a little lighter as the gas passes away and the furnace gets hotter. Thus not only does the operation in the blind furnace last very much longer (say, twice as long), but it does not on an average yield as thoroughly decomposed sulphate of soda as that in open driers. In the latter the operation is only finished when the mass has become red hot all through, and when very little gas comes off it. The salt cake must not be allowed to flux, since this would spoil the quality of the sulphate for ball making.

The yield of furnaced salt-cake from salt of average moisture (say 5 per cent.) is generally assumed at 112 parts for 100 parts of salt. The output of each pan and furnace, with open driers, is rarely below 11 tons per twenty-four hours (counting in the nitre cake from the sulphuric acid

works, which is usually put into the pan along with the salt), and rises up to 14 tons. From blind furnaces it rarely exceeds 8 or 9 tons.

The decomposition of the salt takes place mostly in the pan. About two-thirds of the hydrochloric acid is evolved in the pan, and that principally during the first stage (the "dissolving"), and only one-third or thereabouts in the furnace. In the pan a great deal of sodium bisulphate (hydro-sodic sulphate, $NaHSO_4$) is formed, which in the furnace reacts on the undecomposed sodium chloride, thus—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The decomposition is never quite complete; even weak sulphate contains a little bisulphate (commonly styled "free acid"), along with undecomposed sodium chloride, and in strong sulphate the proportion of it may amount to 1 or $1\frac{1}{2}$ per cent. of SO_3 in the state of $NaHSO_4$ on the sulphate. Salt-cake containing more than this is considered faulty. Strong sulphate ought not to contain more than $\frac{1}{2}$ to $\frac{3}{4}$ per cent. of sodium chloride.

Jones' mechanical furnace is shown in Figs. 6, 7, and 8. Fig. 6 is a section on line A–B Fig. 7; Fig. 7, a plan on line C–D Fig. 6; and Fig. 8, section on line E–F Figs. 6 and 7. This furnace combines the work hitherto done in the decomposing pan and the drying or roasting furnace, and works with a large saving of labour and fuel. It consists essentially of a circular flat pan, 14 to 16 feet in diameter, heated by a coke fire from *above*. In this pan a vertical shaft is set in motion by overhead gear, from which four arms proceed horizontally; and to the latter a kind of knives or ploughs are attached, at varying distances from the centre, so that during the revolution of the shaft every portion of the contents of the pan is kept stirred up. The action is continued till practically all the hydrochloric acid is driven off, and the contents of the pan are then discharged in the state of excellent finished sulphate of soda. A great advantage of this process is this—that if the charge be either too strong or too weak, it can be made quite right at any moment by adding more acid or more salt, as the case may be. In practice, generally an excess of acid is run in at first; and when it has been thoroughly mixed, it is determined by analysis how much salt is required to make the sulphate just right. At present only three charges are worked in twenty-four hours, of about 4 tons of salt each for a 14-feet pan; but it is intended to

Fig. 6.

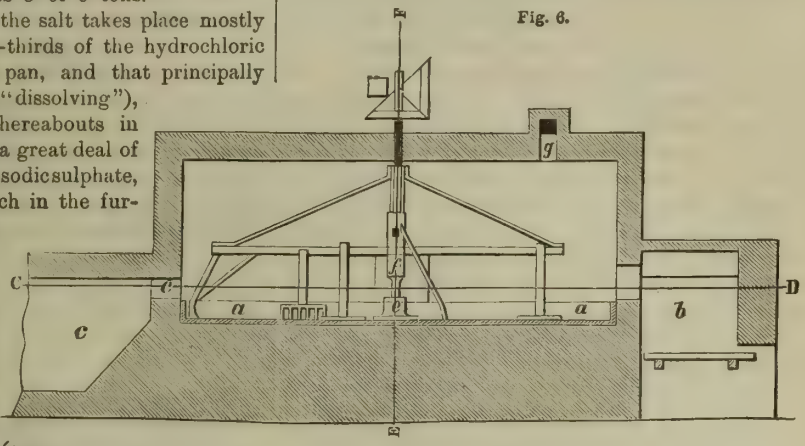


Fig. 7.

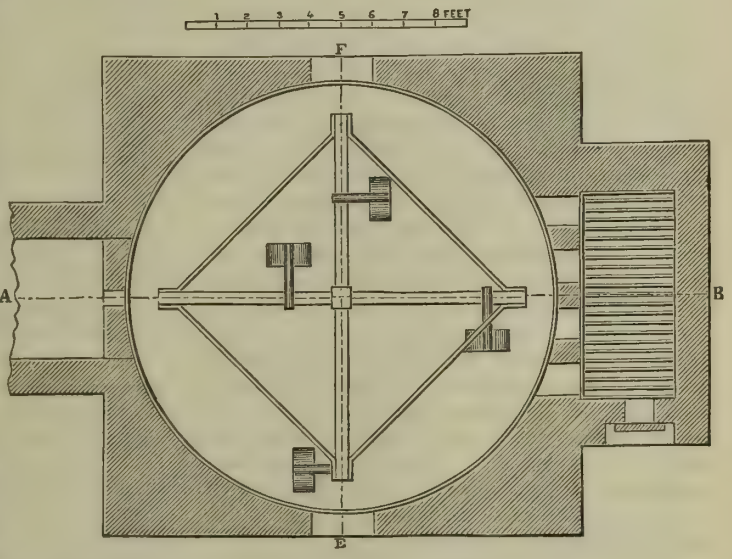
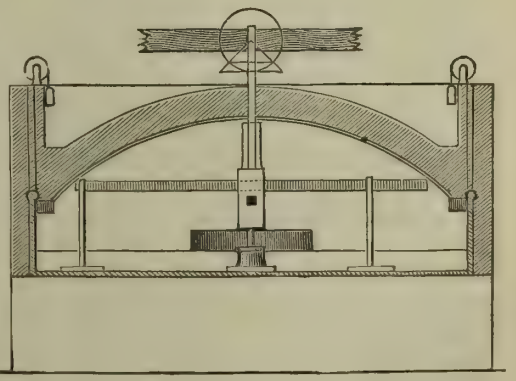


Fig. 8.



fill and discharge the pan automatically in future, which will make it possible to work a charge every six hours, of 5 tons for a 16-feet pan, or 20 tons

of salt per twenty-four hours. This will only require the attendance of one man at a time, against two panmen and two or even four driers on the usual system. The consumption of coke is only 1¼ cwt. per hour, or about one quarter of the fuel in ordinary working; no breakages of pans are to be apprehended, and no skilled labour is required. The condensation of the hydrochloric acid is quite as easy as in the old method, in spite of its dilution with the fire-gases, owing to its more steady and regular evolution. There is no more condensing space than usual for a drier alone, and yet the strength of the acid condensed is 30° Twaddle. This system will probably be very extensively adopted by alkali makers. It will, however, have to be modified in some details, as several alkali works using it have met with important drawbacks to its use. Other mechanical furnaces are those invented by CAMMACK and WALKER, by BLACK and HILL, &c.

The sulphate of soda (called "salt-cake" in Lancashire and Ireland), as drawn from the furnace, ought to show a bright yellow, lemon to orange, colour, which remains till it is quite cold. It ought to be loose and of tolerably fine grain, with few lumps, or only quite friable ones. Undecomposed salt appears mostly in hard lumps, which break up with difficulty, and show a honey-combed grey interior. When the sulphate shows a red colour (from ferric oxide), it is called "burned." This hardly ever occurs, except in the case of weak sulphate. Some alkali makers like it in that state; the majority prefer it in the above-described state, and maintain that "burned" sulphate makes bad balls—probably because it is more difficult to decompose in the ball furnace.

Testing of Sulphate of Soda for Commercial Purposes.—For the interior economy of alkali works, the only points of importance are the "free acid" (really the hydro-sodic sulphate) and the undecomposed sodium chloride. The former is usually expressed in per cents. of SO_3. The testing can be done in a few minutes with sufficient accuracy for that purpose, by adding to a dissolved sample of sulphate standard soda solution from a burette, till a change of colour into brown and a slight precipitation of ferric oxide show that all free acid has been neutralized. The sample is then tested with silver nitrate for chlorides, after adding some potassium chromate. For calcium and iron sulphate, 1½ per cent. are generally assumed. This is, of course, not done for more accurate purposes, when the ordinary analytical methods must be followed.

ANALYSES OF SULPHATE OF SODA (SALT-CAKE) BY G. E. DAVIS.

	A.	B.	C.
Insoluble in water,	0·112	0·073	0·042
Free sulphuric acid,	0·955	1·820	0·022
Calcium sulphate,	1·139	1·148	1·046
Iron persulphate,	0·682	0·588	0·322
Sodium chloride,	2·632	0·234	0·744
Sodium sulphate,	94·393	96·137	97·824
Moisture,	0·987	—	—
	100·000	100·000	100·000

A is from a "blind roaster" (muffle furnace); B, from an "open roaster" (reverberatory furnace); C, was made by HARGREAVES' patent process. The following are—

OLDER ANALYSES.

	Chandelon.			Brown. (English.)
	English. Metal Pans.	Belgian. Lead Pans.		
Sodium sulphate,	93·15	94·10	95·29	96·22
Calcium sulphate,	1·21	0·84	0·86	0·97
Magnesium sulphate,	—	0·35	0·77	0·29
Aluminium sulphate,	0·15	0·16	0·41	—
Ferric sulphate,	0·75	0·97	0·14	0·23
Lead sulphate,	—	—	0·05	—
Sodium chloride,	1·66	0·14	0·37	1·09
Sulphuric acid (SO_3),	1·44	2·52	1·30	0·88
Moisture,	1·28	0·48	0·29	—
Insoluble (sand),	0·26	0·42	0·51	0·31
	99·90	99·98	99·99	99·99

The following perfectly authentic calculation of cost of sulphate of soda in 1874, from one of the largest French chemical works, will present some interest:—

	Francs.			
Labour,	6·17			
Sulphuric acid,	51·39			
Grey salt,	18·91			
Nitre cake,	3·62			
Coal (6 cwts.),	5·42			
Articles in pottery,	0·68			
Sundries,	0·43			
Lighting,	0·12			
Residues,	0·06			
Repairs of buildings,	0·38			
" apparatus,	9·16			
General charges at works,	2·84			
" " Paris,	0·28			
Pension fund (for men of thirty years' employment,	0·55			
	100·01	=	£4	0 0
Deduct value of 1½ ton hydrochloric acid, at 32½ to 34½ per cent.,	30·00	=	1	4 0
Nett cost of salt-cake,	69·81		2	16 0

Each pan and furnace makes 2 tons per day.

Hargreaves' and Robinson's Process.—The sulphate of soda is produced by the direct action of sulphurous acid, oxygen (from air), and steam upon sodium chloride. The gaseous products consist of hydrochloric acid, together with nitrogen and excess of steam. The reaction commences at 750° Fahr., and increases in intensity as the temperature rises. When the supply of sulphurous acid is deficient, the hydrochloric acid in the presence of oxygen is split up into water and chlorine. The reaction occurring when the proper proportions are observed may be represented as follows:—

$$SO_2 + O + 2NaCl + H_2O = Na_2SO_4 + 2HCl.$$

Salt, either in the form of rock or crystal, may be used; but the best results are obtained when finely divided salt is moistened by exhaust steam, which raises its temperature to 220° Fahr.; spread by revolving arms on iron plates, and dried into hard flat cakes, and then cut into pieces about 1½ inches diameter. The iron plates travel slowly through an oven like those used by biscuit bakers.

The prepared salt is placed in iron cylinders, where it is subjected to the action of the gas. The cylinders, not less than eight in number, are arranged in a series, so that each in its turn becomes first, intermediate, and last. The salt lies upon movable grids which are supported on tripods; these being knocked away at the end of the operation, the salt cake falls and is readily withdrawn. The sulphurous acid is first admitted into the cylinder whose contents are most nearly converted into sulphate, and the spent gases pass out from that which was last charged with salt, after passing through a succession of cylinders containing less and less sulphate.

The cylinders are arranged in two rows, and the ground space between them is filled by an arch covered with ashes; the flues from the burners are protected from loss of heat by the arch and the bulk of ashes.

Sulphurous acid direct from the pyrites kiln is found to be too concentrated to be allowed to pass direct into the cylinders containing raw salt, since the action is then so violent as to fuse it into a hard mass. This is the reason that the nearly spent gas is made to play upon the pure sodium chloride and cover it with a coating of sulphate; as the cylinder is brought nearer to the beginning of the series this coating increases in thickness, whilst at the same time the reaction proceeds evenly and regularly.

The cylinders are heated by a small furnace. The hot gases pass through a horizontal flue and ascend narrow vertical flues; these flues are only 5 square inches in section, the object being to reduce the heat-absorbing surface. They are, however, amply large enough to carry away all the products of combustion. After leaving the vertical flues the smoke circulates round the cylinder and charging holes, and passes away to the chimney.

As the heat generated in the process is more than enough to keep up the operation, and the losses of heat are due to radiation and convection from the bounding surfaces of the apparatus, it is evident that as the apparatus is enlarged so as to reduce the relative proportion of bounding surface to cubical capacity, the proportion of fuel per ton of sulphate must decrease also, and it is only a question of carrying the principle far enough, to do altogether without fuel for keeping up the temperature of the cylinders. This has been proved by experience; an early form of apparatus required 2 tons of fuel per ton of sulphate, whereas 3 cwts. of fuel suffice with enlarged cylinders.

The pyrites burners are much like those used in vitriol making; they are placed back to back, and exposure of iron to the direct heating effect of the burning pyrites is avoided as much as possible. The outside walls are 18 inches thick, preferably using 5-inch fire brick lining and common bricks for the outer wall. The rate of conduction of common bricks being less than that of fire bricks, a saving of heat as well as cost in erection is effected. The back of the arch is thrown lower than the front and the gas flue placed in the depression, a wall is raised over the burner fronts, and the entire space over the burner covered with ashes to a depth of 2 feet or more to prevent conduction of heat. The door is protected from the heat radiated from the pyrites by a non-conducting lining.

The steam, before allowing it to mix with the gas from the burners, is superheated to 650° Fahr. by the products of combustion leaving the cylinders, which are at a temperature of about 800° to 850° Fahr.

The hydrochloric acid and excess of other gases are drawn from the apparatus by an aspirating apparatus.

Glauber's Salts—Crystallized Sodium Sulphate—$Na_2SO_4 + 10H_2O$.—A great deal of GLAUBER'S salts is produced by the systematical treatment of sea water, according to the plans proposed by BALARD and MERLE, and carried out to some extent in the south of France. At a low temperature magnesium sulphate and sodium chloride in solution form sodium sulphate, which crystallizes out, and magnesium chloride, which remains in solution. Another large quantity of GLAUBER'S salts is got by working up the "pan scales" of salt works, which consist mainly of sodium and calcium sulphate; by extracting with warm water the gypsum is left behind, to be sold for agricultural purposes, whilst sodium sulphate is dissolved. The lyes are obtained more concentrated by systematical lixiviation, and attain 25° to 26° Beaumé. At that strength they will yield a good crop of GLAUBER'S salts in winter; but in summer they must be concentrated to some extent before they are run into the crystallizing coolers. Before doing so the liquor is purified by settling and filtering through canvas bags. The coolers are long, shallow troughs of wood lined with sheet lead, say 20 feet by 6 feet; the liquor only stands 3 inches deep in them, as otherwise the crystals become too large, which is considered a drawback. As soon as the crystallization sets in, a wooden spade is drawn once from one end of the cooler to the other; this slight motion causes single crystals to be secreted, which afterwards, when quiet is restored, grow principally in their longitudinal axis, and thus acquire that acicular exterior which is expected by the buyers of that article. The liquid must not be moved or stirred about too much; otherwise only very fine crystal "flour" would be obtained. On the other hand, if the liquid is not disturbed at all, the salt is principally formed on the sides and the bottom in the shape of large crystallized masses, which must be chiselled off with a great deal of trouble. When the liquid is quite cool the mother liquor is syphoned off, and a little cold water is poured on the salt with a watering can, in order to wash off the mother liquor. The salt itself is then taken out and dried in the air (in winter in gently-warmed rooms) on wicker-work trays. This drying process must be interrupted the moment any efflorescence shows that it has gone far enough.

A good deal of GLAUBER'S salt is made by dissolving commercial sulphate of soda (made on purpose or brought from alkali works) in water of about 30° C.;

and the solution is at once made strong enough to give a large crop of crystals on cooling.

Before proceeding to consider the manufacture of soda from sodium sulphate, the other product of the action of sulphuric acid on salt will be noticed thus, is:—

HYDROCHLORIC ACID — *Clorhydric Acid*, *Muriatic Acid*, *Spirit of Salt*. Symbol HCl. *Acid Hydrochlorique*, French; *Salzsaüre*, German.

Cl,	35·5	97·26
H,	1·0	2·74
	36·5	100·00

Nearly all the hydrochloric acid now produced in England is obtained from the decomposition of common salt, so extensively used in alkali works, where the acid is chiefly employed for the production of chlorine, bleaching powder, or chlorate of potash. To give some idea as to the enormous extent to which hydrochloric acid is now produced, the writer may mention, that on the river Tyne alone there is produced about 300,000 tons annually, and in the United Kingdom probably altogether not far short of a million tons annually. It may be interesting to glance back for some years to notice how this important branch of manufacture has developed from a very small beginning. As recently even as one hundred years ago chlorine was not used in the arts, and our British-made linens and calicoes, &c., after they were boiled in lyes made from Scotch kelp, were then saturated with sour milk, and were simply exposed for a long time to the action of the sun and air to bleach them. But on account of the uncertain climate of this country it was found to be necessary to send the best cloths to Holland, and after a summer's absence and exposure to a brighter sun, they were returned to England for consumption. White paper suitable to write upon could only at that time be produced from the whitest rags, as no chemical methods for bleaching inferior materials were then in practice. Long before hydrochloric acid was made by the present methods, there is evidence to show that it was occasionally produced by heating clay and salt together in a metal retort, when a small part of the salt was decomposed with escape of hydrochloric acid, or, as it was then called, "marine acid." A nearly similar process was pursued in mixing sulphate of iron (or copperas) and salt, and subjecting the mixture to heat in a retort, when the "marine acid" was also produced (R. C. Clapham).

It was not till about 1789 that this acid began to be produced by the decomposition of salt with sulphuric acid, on a tolerably large scale, and this was first done in France during the French Revolution; but it was not for many years afterwards that hydrochloric acid began to be made in a large way in England. In 1823 the heavy excise duty on salt, which had varied in amount from £10 to £36 per ton of salt, was repealed by the Government, and this at once gave a stimulus to the establishment of alkali works, both on the river Tyne, in Lancashire, and in Glasgow and elsewhere. For several years after the above date there was no extensive use found for hydrochloric acid, and all the fumes from the decomposition of salt were allowed to escape into the air from the short chimneys then in use, and were found to do much injury to surrounding vegetation. At this time, however, the works were comparatively small, and it was not considered necessary to make any attempts to condense the gas; but from the continued increase of demand for alkalies and for bleaching powder the question of condensation became very important and pressing on manufacturers. Various methods were attempted at first. The early experiments in this direction on the Tyne were made at Walker Alkali Works in 1827; large wooden chambers or boxes were erected, through which the gas was made to pass, and in some cases underground cellars or tanks were substituted, and in both jets of water were forced in amongst the gas. In 1835 W. S. Losh, at the same works, put down long underground flues, into which water was forced by means of an engine. The next thing was the erection of towers constructed of stone and filled with glass or flints, through which the hydrochloric (in alkali works always termed *muriatic*) acid gas ascended, at the same time meeting a stream of water; but still for the most part all these attempts were failures, or at least were imperfect, and to get over the difficulty high chimneys were erected, which are to this day a peculiar characteristic of chemical works, the chief object at that time being to spread this injurious gas over a large surface. It was in these difficulties that the late William Gossage, of Liverpool, took out a patent in 1836 for the construction of condensers packed with coke, through which the gas passed, being at the same time subject to a spray or shower of cold water. His method was generally approved by manufacturers, and under all ordinary circumstances these condensers are capable of effecting almost a complete condensation of the hydrochloric acid gas that is now produced so extensively in chemical works. But it was not till 1843 that good condensation was carried out, and it took some years after this date to bring about the perfect system which is now adopted in nearly all chemical works. The escape of small quantities of gas, both from the condensers and the internal arrangements of the works, still, however, continued, and caused considerable damage to the surrounding fields, trees, and gardens.

In 1863 an Act of Parliament was passed, called the "Alkali Act," which fixed the maximum escape of gas from any work at 5 per cent., and at the same time appointed inspectors under the Board of Trade. This Act remained in force till 1874, when a new Act was passed, containing more stringent clauses as to the escape, and fixing the maximum quantity at 0·2 grains per cubic foot of "air, smoke, or chimney gases escaping from the works into the atmosphere." These Acts have now been on trial ever since that time, and no difference of opinion exists as to the advantages which have been derived both by the manufacturer and the general public by their enactment. Much useful information

on condensation has been collected in the able annual reports of the inspectors, and the escape of gas has in each year in all the districts been greatly mitigated.

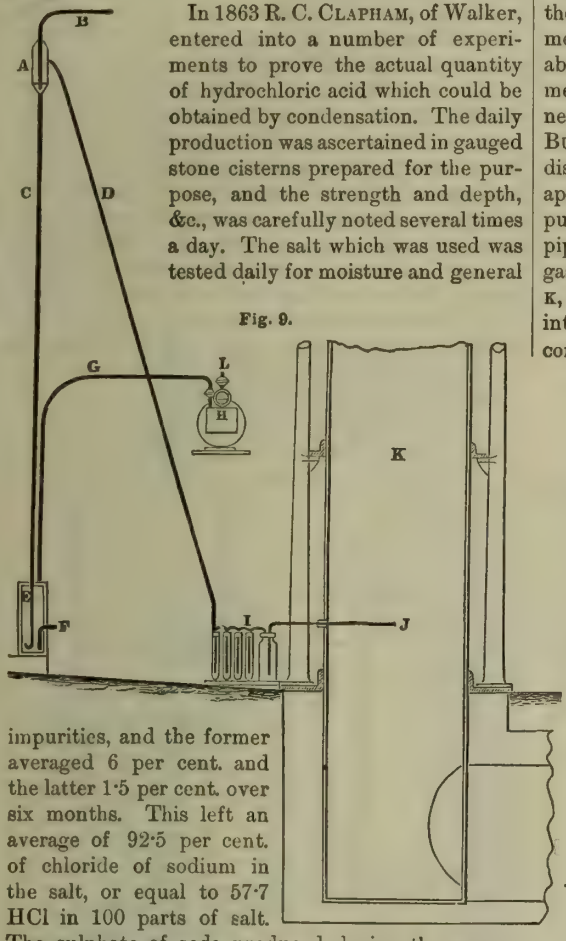


Fig. 9.

In 1863 R. C. Clapham, of Walker, entered into a number of experiments to prove the actual quantity of hydrochloric acid which could be obtained by condensation. The daily production was ascertained in gauged stone cisterns prepared for the purpose, and the strength and depth, &c., was carefully noted several times a day. The salt which was used was tested daily for moisture and general impurities, and the former averaged 6 per cent. and the latter 1·5 per cent. over six months. This left an average of 92·5 per cent. of chloride of sodium in the salt, or equal to 57·7 HCl in 100 parts of salt. The sulphate of soda produced during the experiment was also tested daily, and contained an average of 2·45 per cent. left undecomposed of common salt (NaCl), or equal to 1·52 HCl per cent., which is deducted from the results given below :—

	HCl.
January, 100 parts of salt gave (average),	58·8
February, " "	53·0
March, " "	54·2
April, " "	57·4
May, " "	58·4
June, " "	53·9
Average production of HCl,.....	55·95
HCl left in sulphate of soda,.....	1·52
	57·47
Loss or escape of gas,.....	0·23
Total HCl in salt used,.....	57·70

The above careful experiment, covering six months of full work, equals an average of only 0·398 of HCl in 100 parts of hydrochloric acid in the salt.

J. Mactear, of Glasgow, has given much attention to the question of condensation, and has suggested a continuous method of testing the escape from condensers, of which Fig. 9 is an illustration :—This apparatus consists of an ordinary Bunsen water pump and a wet meter. To get rid of working the meter under the high pressure necessary to suck the gases through the absorbing tubes, the meter measures the gases after they have passed through absorbing tubes and pump, exhausting from the meter into the air. The pressure on the meter is never above a fraction of an inch of water. A is the Bunsen's vacuum pump; B, water pipe to pump; C, discharge pipe from pump; D, pipe to absorbing apparatus; E, trap to collect gases passing through pump; F, overflow pipe for water from pump; G, pipe for conveying gases to meter; H, ordinary wet gas meter; I, absorbing tube; J, glass pipe into flue; K, flue from chambers; L, escape pipe from meter into the atmosphere.

CONTINUOUS TESTS FOR HYDROCHLORIC ACID BY MACTEAR'S PROCESS.

Date.	Grains HCl per Cubic Foot. Day.	Night.	Regular Test, Nine a.m., HCl per Foot.
1876.			
Dec. 18,.....	—	·035	·052
" 19,.....	·064	·022	·055
" 20,.....	·058	·016	—
" 21,.....	·039	·090	·055
" 22,.....	·063	·037	·090
" 23,.....	·074	—	·061
1877.			
Jany. 3,.....	·089	·062	·064
" 4,.....	·075	·060	·084
" 5,.....	·097	·125	·129
" 6,.....	·112	—	·054
			·129
Average, ...	·075	·049	·077

WEEKLY AVERAGES FOR SIX MONTHS.

Date.	Grains HCl per Cubic Foot. Day.	Night.	Average.
1876.			
Dec. 23,.....	·059	·029	·044
1877.			
Jany. 6,.....	·093	·051	·088
" 13,.....	·179	·081	·079
" 20,.....	·103	·054	·080
" 27,.....	·097	·087	·093
Feby. 3,.....	·082	·049	·067
Average escape,	—	—	·075

Week Ending.	Percentage of Acid Condensed.	Week Ending.	Percentage of Acid Condensed.
May 14,....	97·6	Sept. 6,....	97·5
" 21,....	96·0	" 13,....	96·3
" 28,....	96·6	" 20,....	96·4
June 4,....	96·6	" 27,....	96·4
" 11,....	96·2	Oct. 1,....	96·2
" 18,....	96·5	" 8,....	96·7
" 25,....	96·5	" 15,....	96·1
July 2,....	97·0	" 22,....	96 2
" 9,....	96·3	" 29,....	96·4
" 16,....	98·3	Nov. 5,....	97·2
" 23,....	94·8	" 12,....	97·8
" 30,....	96·6	" 19,....	95·8
Aug. 6,....	96·6	" 26,....	95·6
" 13,....	96·4	Dec. 3,....	95·4
" 20,....	96·3	" 10,....	96·6
" 27,....	95·8		

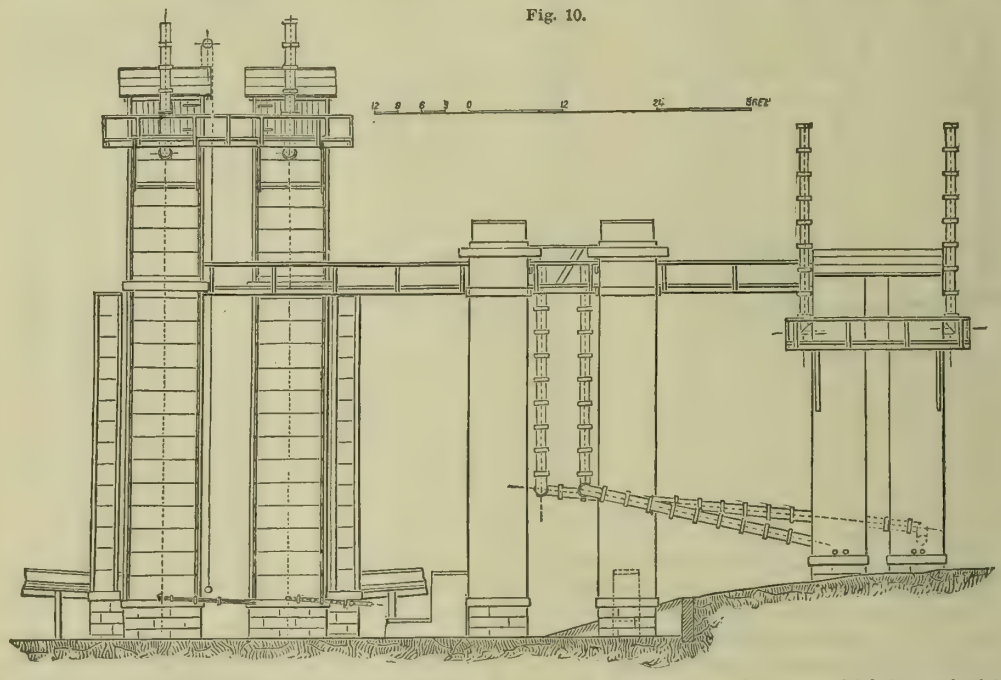
The above table shows the exact amount of liquid

acid obtained in one of the largest works in Lancashire from actual trial. After allowing for 1·6 per cent. HCl left in sulphates, the average escape is 1·8 per cent., and the average acid condensed is 96·6 per cent.

A certain escape of gas always takes place in charging and discharging the furnaces, which has been found by the writer to vary, according to the care taken, from 0·4 to 0·72 per cent. It is very necessary that all condensers should be provided with a supply of water from at least two separate sources, so that in case of accident in the one case, the other can at once be applied.

The size of condensers must always bear a relative proportion to the weight of salt used daily; and as a rule, it is better to have more condenser space than practice actually requires. The plan nearly always adopted in the decomposition of salt on the large scale is to charge the "pan" or pot, which is a metal vessel about 9 feet diameter and 2 feet 6 inches deep in centre, with about 9 cwts. to 10 cwts. of salt per hour, and with rather more than its equivalent of sulphuric acid, which, if possible, should be run into the pan quite warm, and standing about 130° to 140° Fahr. The charge remains in the pot nearly an hour, during which time about two-thirds of the hydrochloric acid passes off to the "pan condenser." The charge is then pushed forward into the furnace, which is kept at a red heat, and where the remainder of the gas (about one-third) is driven off to the "drier condenser." The gases given off from the furnaces, and which passed away to the flue at a high heat, were the chief difficulty to contend with, and were the cause of nearly all the claims for damages made by farmers on the manufacturers in former years. This difficulty has

Fig. 10.



been almost entirely overcome by the adoption of cooling flues or cooling shafts, by which means the gases are considerably reduced in heat before entering the condensers, and a more perfect condensation is obtained. In some works the heat of the gases as they leave the pan and drier are as under:—

Pan gas,	175° Fahr.
Drier gas,	1200° "

By the adoption of a proper system of cooling, the pan gas may be reduced to 120° Fahr. and the furnace gas to under 200° Fahr. before they enter the condensers. During the best condensation, even when cold water is used, there is a certain amount of heat always generated in addition to the heat as it enters, and the escaping steam and gases at the exit pipe seldom stand much less than about one-half of the heat as it enters.

A new decomposing furnace, which is worked by machinery instead of hand labour, has recently been introduced by Jones and Walsh (see *ante.*). The escaping gases from this furnace are generally about one-half the degrees of heat as the ordinary drying furnace, and the condensation is therefore more easily accomplished, and is more perfect. The usual size of a condenser is about 50 to 70 feet high by 6 to 7 feet square, but these proportions vary in different works. They are constructed of stone flags, which are cemented and bolted together; and the condensers are packed with either bricks or coke, through which the gas travels, and is met by a continuous stream of water, regulated at the top of the condensers to suit the strength of acid required and the proper condensation of the gases. In some cases fine spray is thrown in at the foot of the condenser, or in a cistern, from a

"Newall jet," connected to a water supply at a high pressure, and which not only assists the condensation, but also improves the draught. Fig. 10 shows the arrangement of condensers where great care was taken to prevent escape, and where the weak acid from the last towers, which stood about 5° or 6° Fahr., was pumped up to the top of the other condensers, and used in the place of water. In this way all the acid produced was utilized, and no acid was allowed to run into the neighbouring stream or river, frequently causing nuisance and damage.

Fig. 11 also shows condensers, which can be used either for the gas passing from the pan or from the furnace, and where the usual application of water is in operation.

Fig. 11.

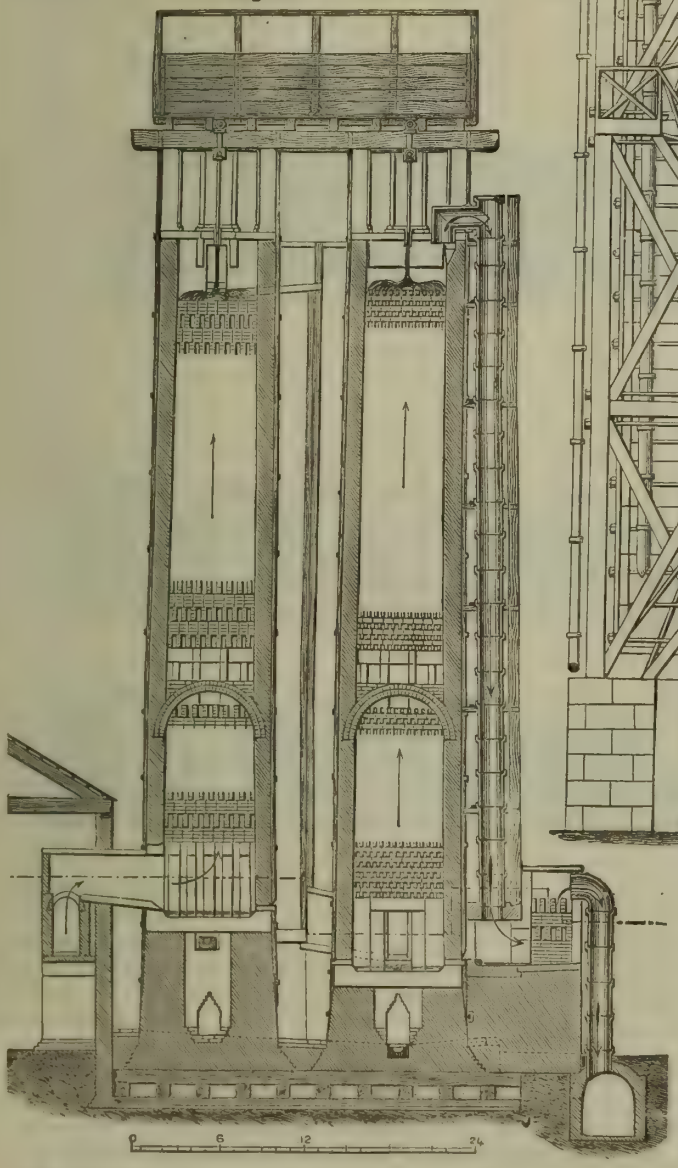
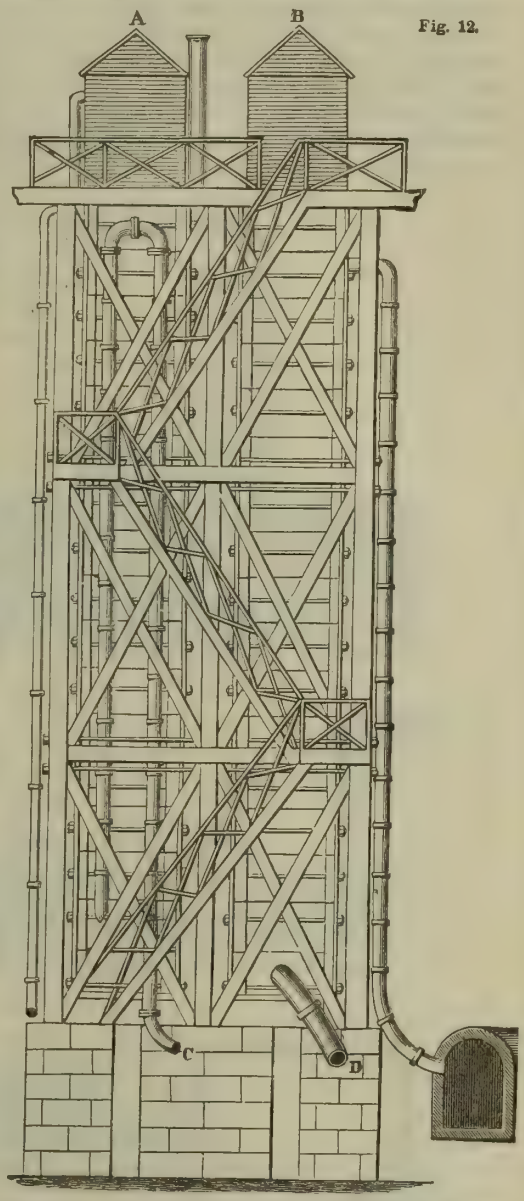


Fig. 12 gives condensers suitable for a pan and furnace working about 8 cwts. of salt per hour. The condenser, A, is connected with the pan, and has a cooling pipe in all about 150 feet long, and is packed with hard burnt coke. B is connected with the furnace or drier, and is packed with bricks, and is worked with an open furnace; the cooling flue (not shown in plan) is about 100 feet long.

Fig. 12.



It may now be interesting to compare the condensing apparatus generally adopted in France. In the first place, the weight of salt for the daily charges is much smaller than in this country, and it is worked off very slowly, with the object of securing a complete condensation of the hydrochloric acid.

The gas is made to traverse an extensive series of Woulfe's fire-clay bottles, which are used instead of the English condenser. The number of these condensing vessels varies in each work according to the salt decomposed, and with a furnace turning out only 2½ tons daily it requires about 100. In the French chemical works much attention is given to the details, and although the acid produced from these vessels is run off at about 30° to 32° Tw. (specific gravity 1·150), a mere trace of gas is found to escape at the chimney. On the whole, it would appear that the cost of condensing plant in France is less than the condensers in England, and the practical results of condensation are favourably shown by the healthy vegetation in farm crops and trees frequently found growing close up to the French chemical works. Figs. 13, 14, and 15 will give an idea of the apparatus in use.

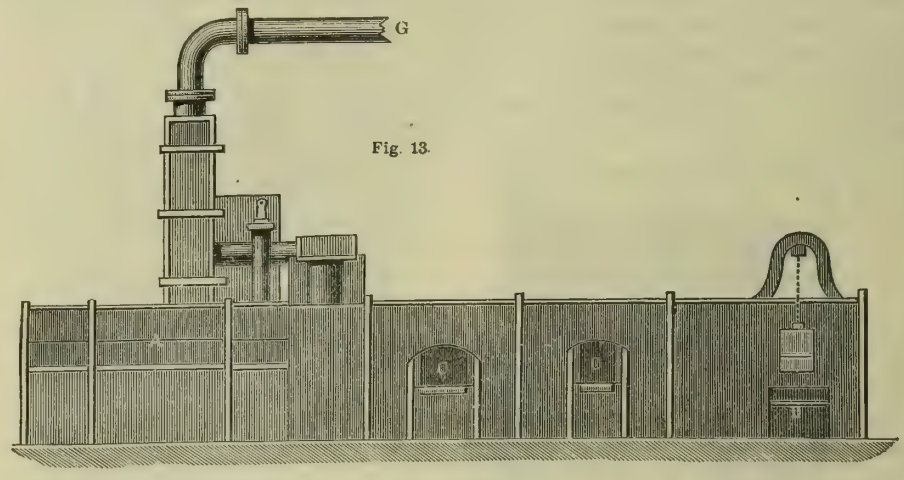


Fig. 13.

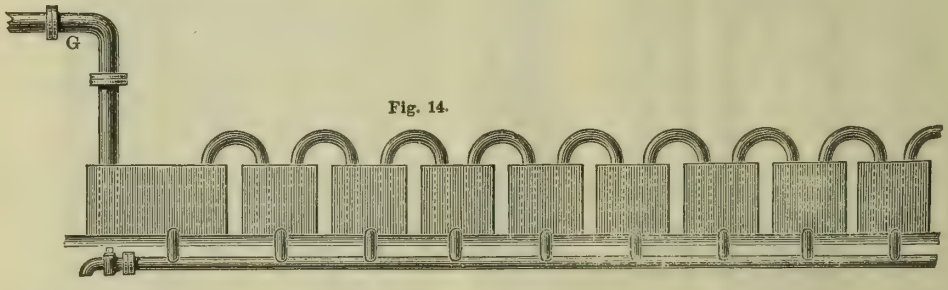


Fig. 14.

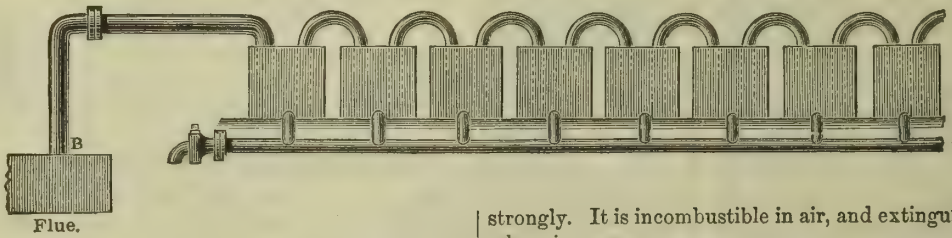


Fig. 15.

A is the decomposing pan, B is a lead pan for sulphuric acid, C, C are the working doors for furnace, D the fire-place, and G the gas pipe.

Properties.—Hydrochloric acid in solution is a colourless fluid. When first formed it is of a pale yellow colour, but becomes quite colourless on exposure to light, a proof that the colour is not essential to it, and may be caused by organic matter, &c. The gas itself is also colourless, fumes in moist air and has a peculiar and suffocating odour, and causes inflammation and itching of the skin. It reddens litmus strongly. It is incombustible in air, and extinguishes a burning paper.

When equal volumes of hydrogen and chlorine are mixed and exposed to light, they slowly combine and produce hydrochloric acid gas; and if the mixture be exposed to the direct rays of the sun, detonation frequently occurs. It also explodes when exposed to the intense light of the voltaic discharge passing between charcoal points; and if the experiment is made in a tube over water, a peculiar vibratory motion of the surface of the water is generally noticed before the explosion takes place (Gay-Lussac). The agency of light on hydrogen and chlorine

may be beautifully shown by filling a tube, about half an inch in diameter and 12 inches long, with the mixed gases, and alternately shading it with an opaque cover and exposing it to the sun's rays; and the moment the tube is exposed even to the diffused light of day, a cloudiness appears within it, and the water ascends more or less rapidly according to the amount of light (HENRY).

DAVY found that the heat evolved during the combination of a mixture of chlorine and hydrogen exceeded that produced by a mixture of oxygen and hydrogen, and that the former was inflamed at a lower temperature. Oxygen and hydrogen ceased to explode when rarefied 18 times, but chlorine and hydrogen retain their combustibility when rarefied 24 times. Hydrochloric acid gas may be decomposed by the action of several of the metals—potassium, for instance, absorbs chlorine and the hydrogen is evolved. This experiment is best made in a small retort, which is exhausted of air, and filled with hydrochloric acid gas from a jar over mercury. When cooled it will be found that the residuary gas is hydrogen, equal to half the original bulk of hydrochloric acid. Tin and lead heated in the gas also effect its decomposition, and evolve exactly half its bulk of hydrogen. The greater part of the metallic oxides when heated in gaseous hydrochloric acid decompose it, and metallic chlorides are formed, and the oxygen of the oxide, combining with the hydrogen of the acid, forms water. Solution of hydrochloric acid was first made known by GLAUBER as far back as the middle of the seventeenth century; but hydrochloric acid gas was first isolated by PRIESTLEY, in 1772. It was procured by acting on common salt with sulphuric acid. The specific gravity is 1·262, and as it consists of equal volumes of hydrogen and chlorine combined without change of volume, 100 cubic inches must weigh 39·36 grains (BRANDE). According to THOMPSON, 100 cubic inches at $0°C_2$ weigh 42·126 grains. FARADAY liquefied this gas by generating it in a sealed tube, so as to expose it to a pressure of about 40 atmospheres at 10° C.; it was colourless, and possessed a refractive power inferior to that of water, but he could not succeed in solidifying it.

Hydrochloric acid has a strong attraction for water; and when it escapes into the air, it forms strong dense fumes, from its absorption of water from the atmosphere (BRANDE).

Water takes up 480 or 500 times its bulk of hydrochloric acid gas, and has its specific gravity increased from 1 to 1·210 (H. DAVY).

Hydrochloric acid gas is rapidly absorbed by water: 100 cubic inches of water will absorb no less than 48,000 cubic inches of this gas, whereby the liquid acquires a specific gravity of 1·210, and a volume of 142 cubic inches. This great condensation is accompanied with a considerable production of heat. In general muriatic acid of commerce has a specific gravity of 1·15 to 1·20, and contains for the most part less than 40 parts by weight of acid in the hundred. In general a very good approximation may be found to the percentage of real muriatic acid in any liquid sample by multiplying the decimal figures of the specific gravity by 200—thus, for example, at 1·162, we shall have by this rule, $0·162 \times 200 = 32·4$ for the quantity of gas in 100 parts of the liquid (Dr. URE).

Uncombined hydrochloric acid exists in small quantity in the human gastric juice. It is not found in nature except occasionally as a volcanic product. The principal uses of this acid are in medicine, in the production of chlorine, and in some of the arts, where it is chiefly used as a solvent for metals. It is extremely injurious to vegetation; and mixed with 20,000 times its volume of air, it proves fatal to plants, shrivelling and killing all the leaves in twenty-four hours (CHRISTISON).

When metallic zinc is put into strong liquid hydrochloric acid, the latter is rapidly decomposed, and the hydrogen copiously evolved may be burned as it escapes. Dioxide of lead added to hydrochloric acid immediately disengages chlorine, which may be shown by its bleaching power upon a piece of paper dipped into indigo blue. These experiments illustrate the separation of two elements in the acid.

Hydrochloric acid may be produced in the laboratory in a glass retort, from a cold mixture of 8 parts of common salt, and 13 parts of oil of vitriol, and 3 parts of water. The retort is connected with a system of WOULFE'S bottles, which are kept cool by being placed in water, and covered on the top with damp cloth or by bibulous paper. In the first bottle is placed a very small quantity of water; in the second, as much distilled water as is equal in weight to the salt used, and the third bottle somewhat less. The retort may be gradually heated on a sand bath nearly to redness; and the solution of acid which collects in the first bottle is generally weak, and contains most of the impurities—such as chlorides of arsenic, iron, &c. The 8 parts of water in the second bottle are converted into 13 parts of hydrochloric acid of specific gravity 1·145. If the sulphuric acid contains any nitric acid, the hydrochloric acid may contain free chlorine. The water in the third bottle absorbs the last traces of the gas, and forms a weak solution, which may be again used in the next operation (GMELIN).

Commercial hydrochloric acid is made on the large scale for employment in the arts; and when a high strength of acid is required, in an apparatus very similar to that described under NITRIC ACID. The salt is decomposed by sulphuric acid in a metal retort, about 6 feet long by 20 inches in diameter; and the hydrochloric acid which is generated is absorbed in a series of earthenware bottles, producing a commercial acid of about 32° Tw., or 1·16 specific gravity. The chief impurities in this acid are chlorides of arsenic (got from the sulphuric acid used), and of iron (from the action of the acids on the metal retort). These impurities are mostly arrested in the first bottle, and the second bottle generally contains a hydrochloric acid nearly pure, and which can be used in medicine and for other purposes where a chemically pure acid is necessary (R. C. CLAPHAM).

The acid made by this process is chiefly manu-

factured in Glasgow, London, and Manchester, and as before stated, forms but a comparatively small part of the total acid produced from all sources. The solid salt left in the retorts is called "salt cake," and is generally sold to alkali-makers, to be converted into carbonate of soda. The following are analyses of this substance taken from a large number of samples :—

	1.	2.	3.	4.
Chloride of sodium,	11·00	6·32	1·48	12·50
Sulphate of soda,	68·19	80·47	79·72	64·41
Free sulphuric acid,	4·98	7·24	10·88	10·71
Silica, &c.,	1·80	0·80	2·00	2·10
Oxide of iron, &c.,	0·30	0·10	—	0·25
Water,	13·01	4·76	5·92	9·52
Sulphates of lime and magnesia,	0·70	0·30	—	0·51
	99·88	99·99	100·00	100·00

(R. C. Clapham).

TABLE OF HYDROCHLORIC ACID, BY DR. URE.

Acid by 120 in 100 parts.	Specific Gravity.	In 100 parts Chlorine.	In 100 parts Muriatic Acid.
100	1·2000	39·675	40·777
99	1·1982	39·278	40·369
98	1·1964	38·862	39·961
97	1·1946	38·485	39·554
96	1·1928	38·089	39·146
95	1·1910	37·692	38·738
94	1·1893	37·296	38·330
93	1·1875	36·900	37·923
92	1·1857	36·503	37·516
91	1·1846	36·107	37·108
90	1·1822	35·707	36·700
89	1·1802	35·310	36·292
88	1·1782	34·913	35·884
87	1·1762	34·517	35·476
86	1·1741	34·121	35·068
85	1·1721	33·724	34·660
84	1·1701	33·328	34·252
83	1·1681	32·931	33·845
82	1·1661	32·535	33·437
81	1·1641	32·136	33·029
80	1·1620	31·746	32·621
79	1·1599	31·343	32·213
78	1·1578	30·946	31·805
77	1·1557	30·550	31·398
76	1·1536	30·153	30·990
75	1·1515	29·757	30·582
74	1·1494	29·361	30·174
73	1·1473	28·964	29·767
72	1·1452	28·567	29·359
71	1·1431	28·171	28·951
70	1·1410	27·772	28·544
69	1·1389	27·376	28·136
68	1·1369	26·976	27·728
67	1·1349	26·583	27·321
66	1·1328	26·186	26·913
65	1·1308	25·789	26·505
64	1·1287	25·392	26·098
63	1·1267	24·996	25·690
62	1·1247	24·599	25·282
61	1·1226	24·202	24·874
60	1·1206	23·805	24·466
59	1·1185	23·408	24·058
58	1·1164	23·012	23·050
57	1·1143	22·615	23·242
56	1·1123	22·218	22·834
55	1·1102	21·822	22·426
54	1·1082	21·425	22·019
53	1·1061	21·028	21·611
52	1·1041	20·632	20·203
51	1·1020	20·235	20·796

TABLE OF HYDROCHLORIC ACID, BY DR. URE.—*(Continued).*

Acid by 120 in 100 parts.	Specific Gravity.	In 100 parts Chlorine.	In 100 parts Muriatic Acid.
50	1·1000	19·837	20·388
49	1·0980	19·440	19·980
48	1·0960	19·044	19·572
47	1·0939	18·647	19·165
46	1·0919	18·250	18·757
45	1·0899	18·254	18·349
44	1·0879	17·457	17·941
43	1·0859	17·060	17·534
42	1·0838	16·664	17·126
41	1·0818	16·267	16·718
40	1·0798	15·870	16·310
39	1·0778	15·474	15·902
38	1·0758	15·077	15·494
37	1·0738	14·680	15·087
36	1·0718	14·284	14·679
35	1·0697	13·887	14·271
34	1·0677	13·490	13·863
33	1·0637	13·095	13·456
32	1·0657	12·697	13·049
31	1·0617	12·300	12·641
30	1·0597	11·903	12·233
29	1·0557	11·506	11·825
28	1·0577	11·409	11·418
27	1·0537	10·712	11·010
26	1·0517	10·316	10·602
25	1·0497	9·919	10·194
24	1·0477	9·522	9·786
23	1·0457	8·726	8·979
22	1·0437	8·729	8·971
21	1·0417	8·332	8·563
20	1·0397	7·935	8·155
19	1·0377	7·538	7·747
18	1·0357	6·345	6·524
17	1·0337	6·745	5·932
16	1·0318	6·348	6·524
15	1·0298	5·951	6·116
14	1·0279	5·554	5·709
13	1·0259	5·158	5·301
12	1·0239	4·762	4·893
11	1·0220	4·365	4·486
10	1·0200	3·968	4·078
9	1·0180	3·571	3·670
8	1·0160	3·174	3·262
7	1·0140	2·779	2·854
6	1·0120	2·381	2·447
5	1·0100	1·984	2·039
4	1·0080	1·588	1·631
3	1·0060	1·191	1·224
2	1·0040	0·777	0·816
1	1·0020	0·397	0·408

The variation in the boiling point, with the density of hydrochloric acid, is shown in the following table by Dalton :—

Specific Gravity.	Boiling Point.	Specific Gravity.	Boiling Point.
	Degrees Fahr.		Degrees Fahr.
1·166	170	1·075	228
1·154	190	1·064	225
1·144	212	1·047	222
1·136	217	1·035	219
1·127	222	1·018	216
1·121	228	1·009	214
1·094	232		

Black Ash Process.—The alkali maker having produced the necessary supply of salt cake proceeds to the first stage in Leblanc's process, which is the making of *black ash* (*ball soda*). The materials for this process are calcined sulphate of soda (salt cake), calcium carbonate, either as chalk or as limestone, and small coal (slack). These three substances have to be fluxed together up to, but not exceeding a certain

point, the exact attainment of which is the goal of the alkali-maker. The raw materials will be first noticed, then the construction of the furnace, and, lastly, the way in which the process is conducted.

The foremost of the three raw materials in this process, sulphate of soda, has been treated of at length before. It need only be said in this place that the sulphate which is most adapted for the balling process contains no more than 1 per cent. undecomposed sodium chloride, and generally from ½ to 1 per cent., or even more, of free acid (the acid is not really free, but exists as sodium bisulphate). Although it would seem at first blush as if it were more rational to use thoroughly calcined sulphate, which is entirely free from acids, all practical men agree that such sulphate, which can easily be recognized by its red or "foxy" colour, from the complete oxidation of its iron salts, does not generally make strong soda ash. The reason of it is probably that, being too much calcined, it forms hard lumps which are not so easily acted upon in the fluxing process. A small proportion of ferric oxide is not of much consequence, provided the subsequent operations are properly carried out; but any larger proportion of calcium sulphate (which may be brought into the salt cake by the rock-salt, if such be used in its manufacture) is extremely prejudicial, because a portion of it enters undecomposed into the black ash, and during the lixiviation reduces its equivalent of sodium carbonate again to the state of sulphate. It is most absurd to say (as is done in some books) that it is useful to leave some per cents. of sodium chloride undecomposed. An alkali manufacturer will always make his sulphate as "strong" (that is, free from sodium chloride) as possible, since he can easily reduce his soda afterwards, if he likes, instead of carrying the sodium chloride through all his processes.

The calcium carbonate is introduced into the process in the shape of limestone (as in Lancashire) or chalk (the universal material on Tyneside). The former is always used in the crushed state, the latter in most factories is also preferred in that state; and it is certain that stronger ash can be made, and less chalk will be used where it is employed, not roughly broken, but crushed under edge-runners or between fluted rolls. The purer the limestone or chalk the better they are. Buxton or Welsh limestone is for this reason preferred in Lancashire, and "London" chalk on the Tyne. By the latter expression is understood the chalk from Greenhithe, Northfleet, and other places in the lower reaches of the Thames; the chalk from near the Medway, from Dover, &c., contains too much silica and alumina, and makes bad ash. The chalk as received from the ships (which always bring it as ballast at very low rates) is frequently very wet, and is not easy to grind in that state, as the edge-runners convert it soon into a thick, tough, pasty mass, without reducing it to a fine state of division. It is therefore usual to dry a portion of the chalk, either by the waste heat of some furnace or in separate furnaces heated by refuse coal, and to mix as much of this dried chalk among the undried as enables the mill to work properly. A proportion of one-quarter to one-seventh of dry chalk is generally used with the damp chalk in this manner. The organic substances frequently occurring in limestone, and colouring it black or blue, are of no consequence, as they act similarly to the coal; magnesia in anything like large quantities makes any limestone unfit for balling, but a slight proportion of it does no great harm. Oxide of iron, silica, and alumina are very deleterious. They act like the same substances in the coal ashes, by forming insoluble double silicates of soda and earthy bases, and troublesome soluble sodium silicate and aluminate. Richardson gives the following analysis of London chalk as used in the Tyne (evidently dried).

Lime,	55·20
Magnesia,	trace.
Carbon dioxide,	42·30
Sulphuric anhydride,	0·29
Sodium chloride,	trace.
Alumina and iron,	0·68
Sand,	2·08
Water,	0·30
	100·85

CLAPHAM (ANALYSIS OF UNDRIED CHALK).

Carbonate of lime,	78·000
Sulphate of lime,	0·244
Silicate of lime,	0·325
Phosphate of lime,	0·119
Chloride of sodium,	0·163
Magnesia,	trace
Alumina,	0·220
Oxide of iron,	0·200
Oxide of manganese,	0·150
Silica,	0·600
Water,	20·600
	100·621

Limestones, used in Lancashire, analyzed by G. E. Davies:—

	Buxton.	Minera.	Ruthin.
Organic matter,	traces.	traces.	traces.
Silica,	0·106	0·442	0·398
Alumina,	0·123	0·145	0·135
Ferrous carbonate,	0·187	0·348	0·252
Calcium carbonate,	99·372	98·298	98·370
Magnesium carbonate,	0·116	0·756	0·756
Manganese carbonate,	0·013	0·022	0·026
Calcium phosphate,	trace.	trace.	trace.
	99·917	100.011	99·937

This is, however, only the composition of pure lumps of the above; the crushed limestone, as used in the works, contains more clay, sand, and other foreign matters.

The quality of the coal (slack) used for the soda mixture is of very great importance. Manufacturers like to use always the same kind of coal which they have proved by experience to make good ash, and to which they and their men are accustomed. Whenever they have to try a new kind of mixing coal it happens only too often that something will go wrong, and that bad balls, bad liquors, and low strength ash will be the result. The very first requirement in a mixing coal is that it should be as free from uninflammable substances (ash) as

possible. The more ash, the more silica, alumina, iron, &c., will be introduced into the black ash, all of which in the lixiviation cause a loss of soda ash. Experience has shown that a good mixing coal ought not to contain beyond 7 to 10 per cent. of incombustible substances, certainly not exceeding 12 per cent. Some collieries produce coal better fitted for soda making than others, with no more ash; and it appears on the whole that a coal is the better fitted for mixing the more bituminous substances it contains. "Gas coals" are therefore preferred for this purpose. Bituminous mixing coal becomes semi-fused, and greatly assists the furnace operations; but some alkali-makers believe that more per cent. is used of this kind of coal than of coals containing a larger amount of "fixed" carbon.

Leblanc prescribed wood-charcoal, but this is nowhere used now; and Kolb has shown by trials on a large scale that any substance rich in carbon may be substituted for it, such as coke, sawdust, tar, and peat, all of which simply act in the proportion of their carbon, or rather of their reducing properties, as shown by Berthier's methods, carbon and hydrogen, both acting in the black-ash process exactly in the same proportion as in reducing litharge to metallic lead. It is therefore quite right to use the cheapest source of carbon, that is coal, but as free as possible from iron pyrites and incombustible matter.

Richardson gives the following analysis of mixing coal used on the Tyne:—

Carbon,	74·34	Sulphur,	1·39
Hydrogen,	4 96	Ash,	7·73
Nitrogen,	1·42		
Oxygen,	10·16		100·00

G. E. Davies gives the following full analysis of small coal (slack) used for ball mixtures in Lancashire:—

	Per Cent.
Sulphur,	1·432
Ash,	10·000
Carbon,	70·122
Nitrogen,	0·286
Combustible matter,	88·590
Volatile sulphur,	1·387
Silica,	4·936
Alumina,	2·575
Iron peroxide,	1·511
Lime,	0·700
Magnesia,	0·052
Sulphuric anhydride,	0·243
Phosphoric do.,	0·006
	100·000

Slack is, however, generally only examined for ash, sulphur, and moisture:—

	Ash.	Sulphur.	Moisture.
1.	4·46	0·724	2·41
2.	5·77	0·986	1·00
3.	7·41	0·937	10·14
4.	10·84	1·116	4·72
5.	10·96	1·736	5·11
6.	13·42	0·543	2·98
7.	16 76	0·431	1·22
8.	28·96	1·774	5·44

The nitrogen, which hardly ever fails to occur in the mixing coal, is always more or less injurious in its effects. So far as it escapes in the form of ammonia during the balling process, and during the cooling of the balls, it is harmless; but another portion forms sulphocyanides and cyanides, the latter being transformed during lixiviation into ferrocyanides.

It is not usual to go to any great trouble in mixing the three ingredients of black ash. In most works they are tipped one after the other in front of the ball furnace, and only mixed to a slight extent in shovelling them in; or else into the hopper on the top of the furnace, whence they fall down into the back-bed. In some works a little more is done, by passing the mixture between fluted rolls before it is charged into the furnaces. In no case should the mixture be finely ground, but the fragments ought to remain somewhat coarse, so as to keep the balls more "open" or porous.

The proportion in which the three ingredients of the ball furnace are used cannot be laid down in a completely fixed formula, since very much depends upon the quality of the materials. On the Tyne it is usual (except in one or two works, where larger charges are made) to use for each charge of a "hand" furnace ("revolvers" will be treated of later on) 3 cwts. of sulphate of soda; and this is also the case in the majority of Lancashire works, only a few works making smaller balls (from $2\frac{1}{2}$ or $2\frac{3}{4}$ cwts. of sulphate). The charge of chalk required for 3 cwts. of sulphate varies from $3\frac{1}{2}$ to $3\frac{3}{4}$ cwts., according to the more or less damp state of the chalk; that of limestone (which is practically dry to begin with) varies only from 3 to $3\frac{1}{4}$ cwts.* For reasons afterwards given, it is requisite to confine the proportion of carbonate of lime to the lowest limit which allows the workman to work his ball properly without burning it, and a practised eye can easily tell by the colour of the ball whether to use any less chalk in the next charge or not. The same observation applies to the coal, but in this case it is not the object of the alkali-maker to reduce the quantity; but, on the contrary, to use as much as can be thoroughly incorporated with the fluxing mixture; for only thus an approximately complete decomposition of the sulphate can be brought about, and the ball be kept porous. When too much coal has been used in the mixture, the workman soon finds it out by the fact that his ball works too "stiff," or "dry," or "fiery," and does not "clear;" whilst the foreman or manager perceives it by the unconsumed lumps dispersed through the substance of the ball on breaking up the latter. Different kinds of coal require different proportions; and whilst in some cases the proportion is as low as $1\frac{1}{4}$ cwt. to 3 of sulphate, in others it is as high as 2 cwts. to 3 of sulphate. On the Tyne, with moderately good mixing coal, it does not vary much—about $1\frac{1}{2}$ cwt. The coal is never crushed, but always used in the state called "small coal" in the East, or "slack" in Lancashire

* The larger proportion is mostly used when the black ash is intended for the manufacture of caustic soda.

—that is to say, as a coarse powder, not generally containing any pieces above the size of a walnut. A few manufacturers work with "duff"—that is, the fine dust screened off even of the "smalls," but this is generally considered too impure for use as mixing coal.

With these figures (given from the writer's practical experience) should be compared the statements of different authors. It will be found that the proportions given by Leblanc himself—viz., 1000 parts each of dry sulphate of soda and of carbonate of lime, along with 500 parts of charcoal—agree very nearly with what has been stated above as the mixture generally used in this country, and the following are some of the mixtures recommended by several more modern authors:—Payen (see below) gives a proportion of 100 : 105 : 51; Scheurer-Kestner (*Rép. de Chim. Appl.*, 1862, p. 231) gives the mixture of ten works, where the carbonate of lime (upon 100 sulphate) varies from 90·2 to 121, and the coal from 35 to 73. In three German works mentioned by B. Kerl the proportions were 100 : 115 : 30 to 35, 100 : 121 : 46·6, and 100 : 115 : 68. All these differences testify more to a difference in the raw materials than to anything else. Two figures mentioned by Knapp as the proportions of some German works—viz., 100 : 108 : 183, and 100 : 104·7 : 170·8—seem to contain some mistake in the figure for coals.

If the furnacemen had their own way, they would use as much limestone or chalk as possible, as they could then fire the balls much more without making them "red," and thus be saved the labour of working them thoroughly; but it is the manager's business to cut the limestone or chalk down to the lowest possible limit, as he will undoubtedly get a larger yield by doing so, and have less caustic liquors as well. On the other hand, the men dislike to use much coal, because they cannot "clear" their balls so easily; whilst the manager wants them to use as much coal as can be fairly incorporated in the ball, so as to insure a complete decomposition of the sulphate of soda.

The experiments of Kolb (1866) are among the most important ones in this respect. According to the equation,

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2,$$

the proportions of pure sodium sulphate : calcium carbonate : carbon ought to be as 100 : 70·4 : 16·9 (yielding in theory, 74·6 Na_2CO_3), whilst in practice a large excess of the two latter ingredients is employed—roughly speaking, Leblanc's proportions (100 : 100 : 50) are still in use. Kolb made a large number of comparative experiments on a large scale, at Kuhlmann's works at Amiens, with different proportions, and treated the black ash obtained exactly in the same way. The following table shows the results:—

	Mixture Employed.	Obtained.			
		Na_2CO_3. Na_2O.		Na_2S.	Na_2SO_4.
1.	Na_2SO_4 + $CaCO_3$ + 2C—				
	Sulphate, 106 parts = 100 Na_2SO_4	38·20	3·10	·55	48·51
	Chalk, .. 84 " 70·4 $CaCO_3$	= 43·5 Na_2CO_3			
	Coal, .. 20 " 17 C				
2.	Na_2SO_4 + $CaCO_3$ + 4C—				
	Sulphate, 106 parts = 100 Na_2SO_4	59·51	3·39	2·16	6·71
	Chalk, .. 84 " 70·4 $CaCO_3$	= 65·3 Na_2CO_3			
	Coal, ... 38·4 " 33·8 C				
3.	Na_2SO_4 + 1½ $CaCO_3$ + 4C—				
	Sulphate, 106 parts = 100 Na_2SO_4	63·50	3·80	1·20	6·40
	Chalk, .. 101 " 94 $CaCO_3$	= 70·0 Na_2CO_3			
	Coal, ... 38·4 " 33·8 C				
4.	Na_2SO_4 + 1½ $CaCO_3$ + 4½C—				
	Sulphate, 106 parts = 100 Na_2SO_4	64·20	4·72	1·12	2·06
	Chalk, .. 101 " 94 $CaCO_3$	= 72·3 Na_2CO_3			
	Coal, ... 53 " 44 C				
5.	Na_2SO_4 + 1½ $CaCO_3$ + 6C—				
	Sulphate, 106 parts = 100 Na_2SO_4	52·60	8·45	·15	·93
	Chalk, .. 116 " 103 $CaCO_3$	= 67·0 Na_2CO_3			
	Coal, ... 73 " 50 C				

It will be seen that of mixture No. 1 nearly half the sulphate remains undecomposed, whilst the yield of available soda is correspondingly small. The latter is increased in Nos. 2, 3, and 4, but falls again a little in No. 5, where in consequence of the excess of chalk the caustic soda increases. No. 4 seems to be the most advantageous mixture; but the difference, both in materials and in the style of work, will cause deviations from it in different factories. The excess both of chalk and coal produces an increased yield of soda, because thus the points of contact with the sodium sulphate are increased, and a more complete decomposition of the latter is insured.

Working.—The sulphate of soda, carbonate of lime, and coal are always brought together in *reverberatory furnaces*, called *ball furnaces or black-ash furnaces;* but there is a great difference on this point, whether the operation takes place by manual labour, as in the old furnaces, or by mechanical assistance, as in the "revolvers." We shall first describe the old furnaces, which even now are used in all small works and are not quite extinguished even in large works, although their disuse is only a question of time, as will be seen later on when the advantages and drawbacks of both kinds of furnaces are weighed together. But it is almost equally sure that in the smaller alkali works (and nearly all continental works belong to

this class), the hand furnaces will continue to hold their ground.

The diagrams on Plate III. represent working drawings of a *hand ball furnace* of the very best construction as used on the Tyne. There are, of course, minor deviations in details in every factory, but the principle is always the same. At one end is seen the fire-place, which is generally from 2½ to 3 feet wide, and from 5 to 6 feet long. The fire-bars are plain wrought-iron bars, 2 or even 3 inches square, resting loosely on three horizontal bearers, which are either formed by strong bars laid on one edge, or by strong railway plates. Another horizontal bar is often inserted lower down, to form a rest for the poker during the laborious operation of "scarring" the fire at the end of the shift.

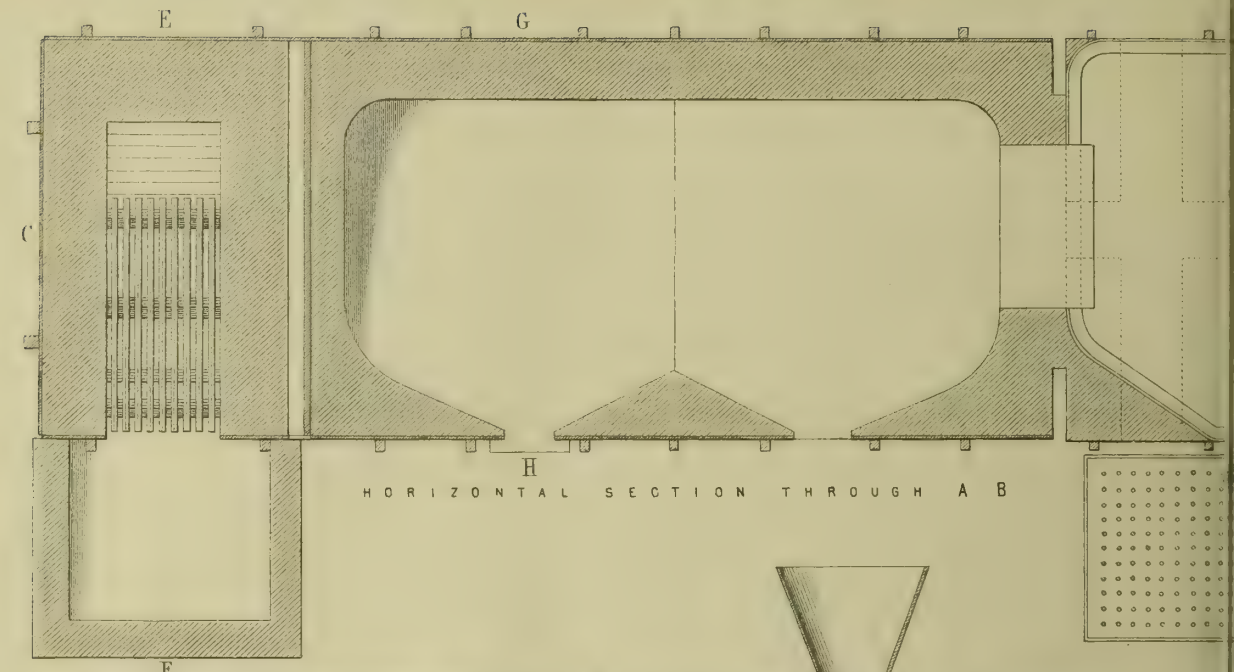
The above simple and somewhat rough arrangement is preferred to any complicated system of fire-bars and fire-places; because the latter are found to give way very soon in actual work, through the "scars" or "clinkers" of the coals adhering to the bars. In the above arrangement of loose bars the "scars" can be removed from time to time by shifting the bars and working the large pieces down into the ash-pit by means of large pokers and scar-hooks. This operation is greatly facilitated by the "cave" under the fire-place shown in the diagram. This is not used in all factories, but only in a portion of them; but the writer can testify to the great advantage of using it, not only in the above respect, but in several others. There is always a water-tap near the cave to quench the ashes and "scars," and to keep the grates comparatively cool; and the cave allows the water to stand regularly in the bottom of the fire-place. The back of the fire-place is frequently stepped back, as shown in the plate, so that the flame can travel along the whole length of the fire-bridge. The latter is a very important part of the furnace; it must be very strong in order to resist the burning coal on the one side, and the fluxing ball-mixture on the other side. The latter penetrates deeply into the furnace beds, and would soon flux away into the fire-place and stop up the latter, if no precaution were taken against this. The precaution consists in building a strong cast-iron plate (1½ to 2 inches thick) in the fire-bridge, which dams back the fluxings, and does not allow them to pass; and as the "bridge-plate," as it is called, would soon be melted or burnt in its own turn, if it were simply put in a solid wall, it is protected by an air-course on the side next to the fire-place. The great heat within the bridge continually causes a flow of cold air to rush into the air-course, and thus preserves the plate for a very long time. Many attempts have been made to utilize this heated air, by conducting it into the inside of the furnace or the fire-place, and in theory this is no doubt an excellent thing, as the heated air will give a much hotter flame than the cold air entering through the grate bars; but unfortunately all such attempts have failed, because the openings, through which the heated air is to escape, are soon fluxed up or blocked up by dust.

The real working part of the furnace is generally divided into two beds, as in the Plate, rarely into three. It is formed by building a 9-inch wall of the very best fire-brick from a depth of 12 inches below the first or working bed, to a height of 15 or 18 inches above the same; this wall goes all round the inside of the furnace, and follows the curved lines shown in the horizontal section. Its left side forms part of the fire-bridge, its back the lining of the furnace back, and its front is pierced for the two working doors. Within this wall is put a layer of ground fire-clay or of dried and ground chalk, 3 inches deep, leaving 9 inches to the top of the bed. These 9 inches are taken up by a course of the hardest fire-bricks on end, wedged closely together without any mortar, and only grouted in at the top with fire-clay. This 9-inch course forms the working bed proper; it is always sloped a few inches from the back towards the working door. The back bed, or "shelf," is a few inches higher than the working bed, and is sometimes only formed of bricks on edge, 5 inches thick. The corners of the furnace, and more particularly its front part altogether, are bevelled off, so that the men can reach every part of the bed with their tools. The doors (both of the fire-place and of the beds) are sometimes only closed by loose iron plates; but it is much better to provide them with fire-clay lumps, inclosed by an iron frame and hung from pulleys with balance weights. The arch of the furnace is generally more or less sloped towards the end of the furnace. The furnace is, of course, strongly bound with uprights (mostly formed by double-headed railway rails) and cross-rods; the upright binders are sometimes let a certain depth into the ground; sometimes, however, they are connected at the bottom by cross-rods as well as at the top, and channels are left in the brick-work for that purpose. In some cases the cross-rods pass through the upright binders; they are then screwed at their ends and fixed with nuts; in other cases they are formed into loops, and driven on tight by means of iron wedges. In a few cases strength is sacrificed to ornament, by making the uprights no higher than the furnace walls, and bending the rods along the crown of the arch. The construction which is shown in Plate III. is much stronger and also more usual.

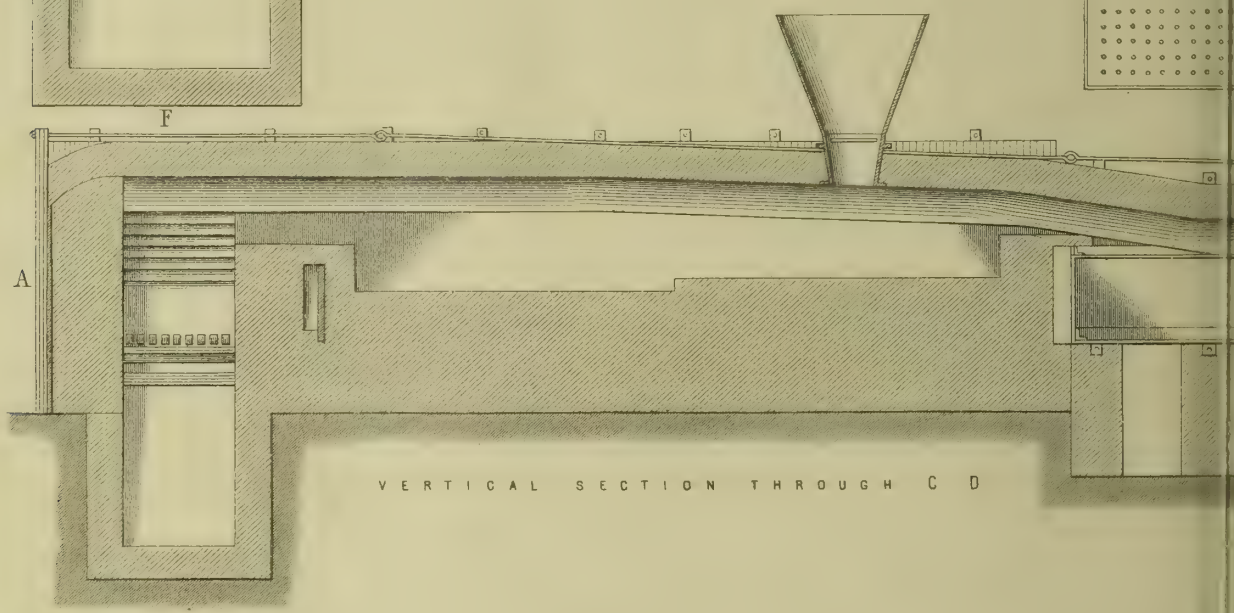
On the Tyne it is usual to case the whole furnace, back, front, and end, with 1 inch metal plates, whilst in Lancashire only small strips of iron (5 inches × ¼ inch), are placed behind the binders. The former plan is of course much stronger; and although more costly in the first instance, it is cheaper in the end, as the plates last nearly for ever, and the furnaces stand much longer.

In Plate III. a hopper is shown over the working bed, through which the ball-mixture is introduced into the furnace. This presupposes an arrangement of over-head tramways for charging the furnaces; where such an arrangement does not exist, the ball-mixture is charged by shovelling it in through the door of the back-bed. This causes more labour, takes more time, and cools the furnace

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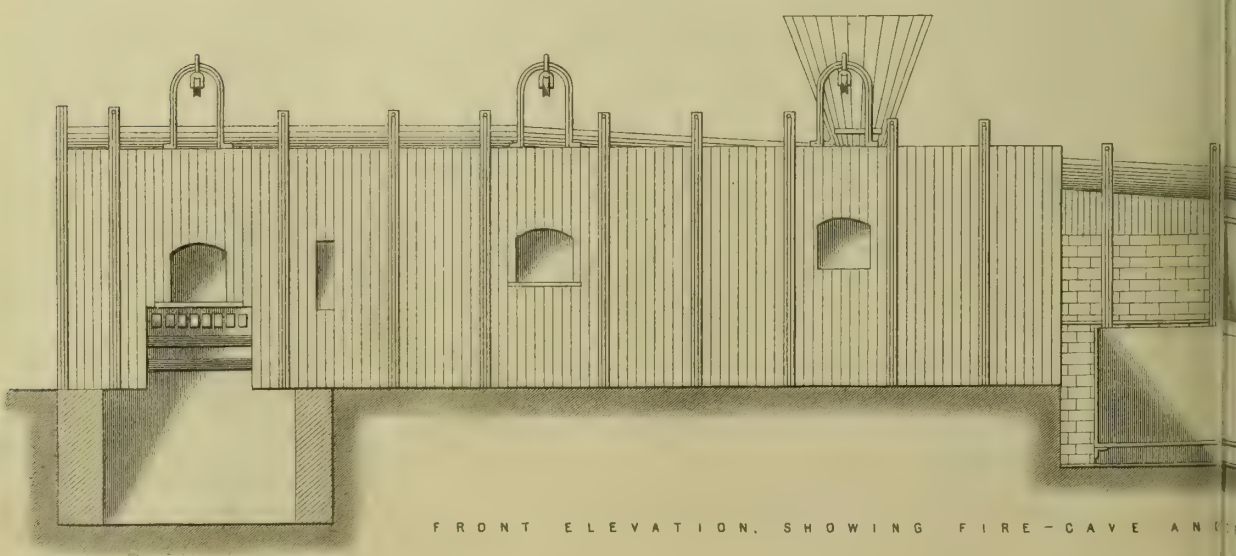
HORIZONTAL SECTION THROUGH A B



VERTICAL SECTION THROUGH C D

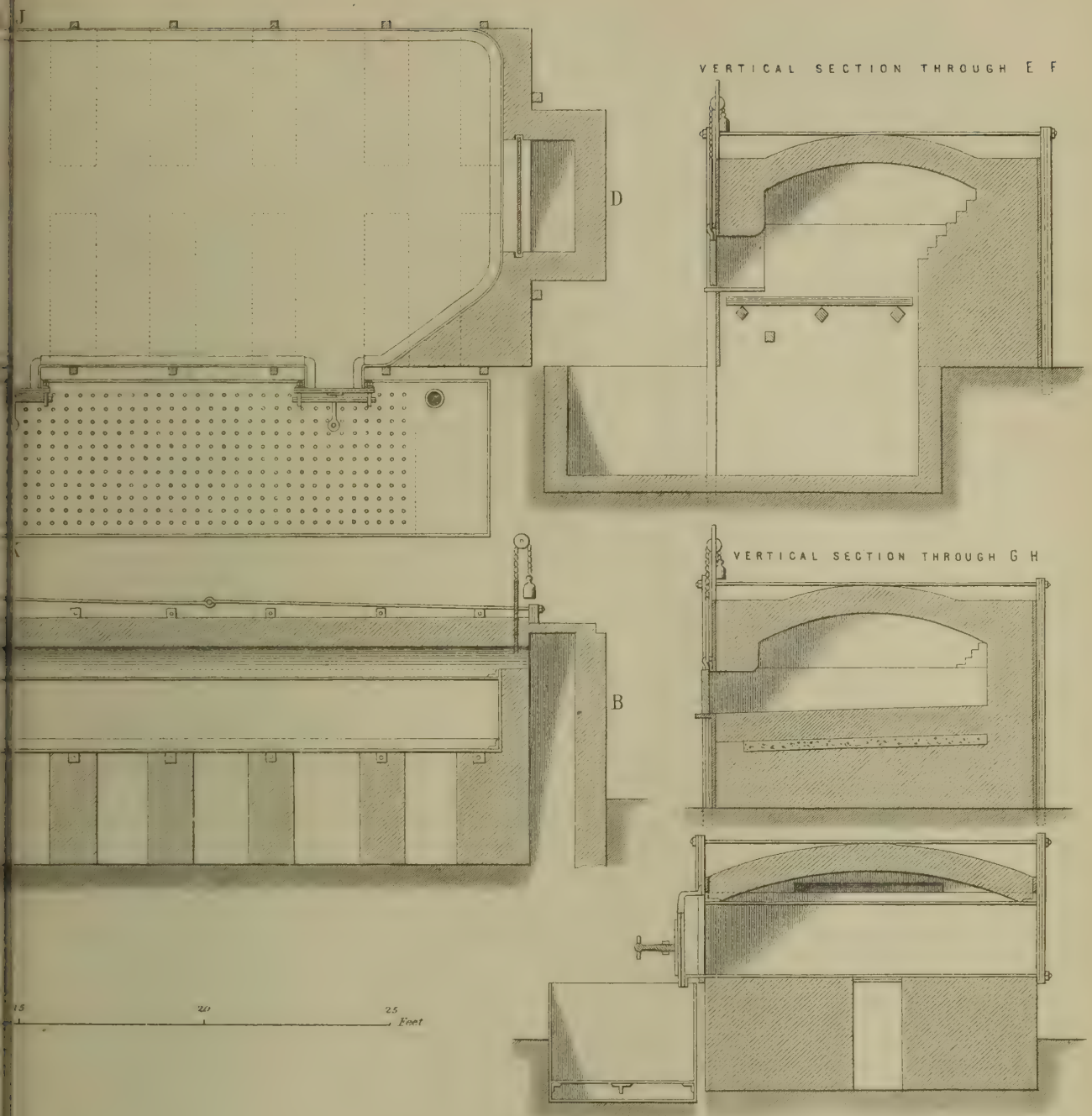
SCAL





FRONT ELEVATION, SHOWING FIRE-CAVE AN

R N A C E & P A N .



RAINER IN SECTION.

GO. PHILADELPHIA.

more than charging by hopper, which is always decidedly preferable where it can be applied.

The size of bed shown in Plate III. is that most usual on the Tyne; in Lancashire the bed is generally much larger, and is especially deeper from back to front. It is also often preferred in Lancashire to build two small fire-places at the end of the furnace, their bars running parallel with its longest dimension, instead of the one large fire-place with bars running across, as shown in the diagrams. In that case there is often a metal plate put in across the fire-end of the furnace, 2 feet deep, having a number of perforations 3 inches in diameter, with a corresponding number of holes ("pigeon holes") in the inner fire-brick casing. These holes serve to admit a further quantity of air to the burning fuel, apart from what enters through the grate-bars; and this arrangement is found to cause a very sharp and steady heat just over the fire-bridge, besides saving a good deal in wear and tear of the fire-bars.

It is hardly necessary to say that all parts of the furnace which come into contact with the fire or ball-mixture must be made of very good fire-bricks. It is usual to make this fire-brick lining 9 inches thick all over; even with this thickness it does not last many months in the more exposed places, such as the fire-hearth, the fire-bridge, and the working bed. It is not only the heat, but the action of the alkali, and, in the case of the bed, that of the tools, which destroys the fire-bricks. They ought, therefore, to be as hard and well burnt as possible; porous bricks are more easily penetrated and dissolved by the alkali (at the same time making the latter impure), and worn away by the tools. The less sand they contain the better, as it is more liable to be acted upon by the fused alkali than the aluminium silicate.

The ball-furnace requires for its proper work a degree of heat approximating (although not quite reaching) white heat, and naturally a vast amount of it escapes unused through the "snore-hole," or over the end bridge, behind the back bed. This waste heat is utilized in boiling down the solution of soda obtained in the process of lixiviating the black-ash; but not always in the same manner. In all factories on the Tyne, and in some of those in Lancashire, the liquors are contained in "open" pans, where the fire is carried along the surface of the liquid, and the evaporation consequently is increased by the draught carrying away the vapour; whilst the salt, as it crystallizes out of the more and more concentrated solution, falls to the bottom and accumulates till it reaches to the top, and the whole is converted into a mortar-like mass, which is pulled bodily out of the pan and allowed to drain in an iron drainer furnished with a perforated false bottom, as shown in Plate III. The pans are made of three-eighth inch iron, of about the same width as the furnace, from 16 to 20 feet long and from 1 foot 6 inches to 2 feet 6 inches high; sometimes they are made to slope towards the front. They are supplied with two or three drawing doors, the form of which can be seen from the diagrams. The doors themselves are pressed against the angle-iron rim, which runs all round the opening of the pan, by means of a strong screw or by wedges, after a layer of good clay, or sometimes of lime, has been put in between. This is sufficient to make the joint tight, and a slight leakage is not of very much consequence, as the necks of the drawing openings reach over into the drainer, so that any escaping liquid is saved there. The angle-iron must not stand up in the opening at all, as it would otherwise be impossible to drain all the contents of the pan. The plates are put together in such a manner that the joints all run at right angles to the doors (across the width of the pan), and they are overlapped on each side towards the doors; the object being that the men's tools when raking out the pan shall not be stopped by any joints. For the same purpose it has been sometimes thought necessary to countersink the rivets; but this is rarely done now. An angle-iron runs round the top of the pan, which not only stiffens the same, but also serves as a hold for the arch covering the pan, between which and the liquor the flame has to travel. The arch is often only 5 inches thick; but it is much better to make it 9 inches, as in the Plate, although this involves some extra plates along the sides of the pan to strengthen the "spring" of the arch. A 9-inch arch is both stronger and keeps the heat much better together than a 5-inch one. The pan is not set immediately at the end of the ball-furnace—it would in that case very soon burn down at that side; but an air course is left along its ends, and fire-clay lumps are laid over this, projecting several inches into the inside of the pan, so that the fire shall not destroy the top of the plates where they are bare of liquor. The pans ought always to be set on pillars in such a manner that the space underneath is accessible. In that case any leakage can be detected before much harm is done, and there is much greater accessibility for repairs when these have become inevitable.

This, then, is the system of open pans. The fire is more efficient in them; they do more work and last longer than pans heated from below; but the salt in them is necessarily contaminated by the products of combustion, and it does not pay to work them except by boiling down the whole contents to a pasty mass. In several Lancashire pans this is avoided by allowing the furnace gas to heat pans *from below*. These are now generally made of the shape called "boat pans," from the fact of their transverse section having some similarity to that of a boat with sloping sides, as will be seen from Figs 16 to 22. Fig. 16 is a section of Wrong's iron boat pan; Fig. 17 a front elevation of the same; Fig. 18

Fig. 16.



a plan of the same; Fig. 19 is a section of a cast-iron boat pan; Fig. 20 is a side section of the same; Fig. 21 a plan of the same; Fig. 22 the mode of set-

ting boat pans. The bottom is purposely set on a brick-wall, and not touched by the fires, so that the salt may quickly accumulate in it and be "fished" out. The fished salt is much purer than the "drainer

Fig. 17.

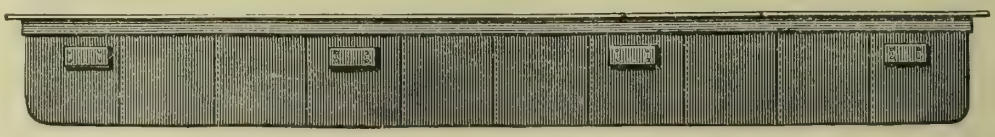
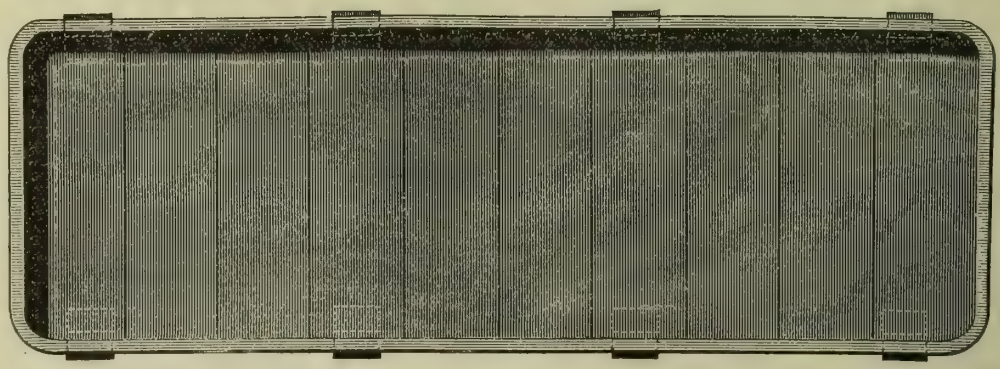
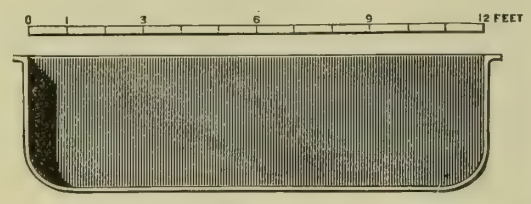


Fig. 18.



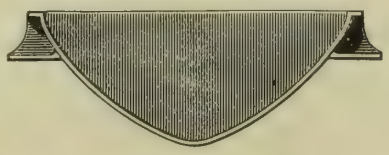
salt" of open pans, as will be seen hereafter, and the residue is worked up either into caustic soda or into "caustic ash."

Fig. 19.



Sometimes the ball-furnace fire first travels over an open pan and then under a boat pan; or, more frequently, under two boat pans in succession. Those boat pans used in connection with ball-furnaces are sometimes made of cast iron, sometimes of wrought iron. The pan furthest from the furnace

Fig. 20.



is placed about 6 inches higher than that nearer the furnace, and the bottom of the latter corresponds in height with the summit of the black-ash furnace arch. One continuous 14-inch wall, on which the bottom of the pan rests, sustains the principal portion of the weight of the latter; while two other 14-inch walls at the front and back (forming continuations of the former wall), built up to the flanged tops of the pans, support their two sides. These three longitudinal walls form between them two flues through which the black-ash furnace fire passes. In order to force the fire nearer to the pans several

Fig. 21.

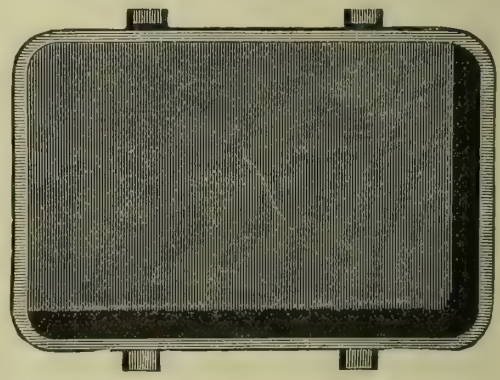
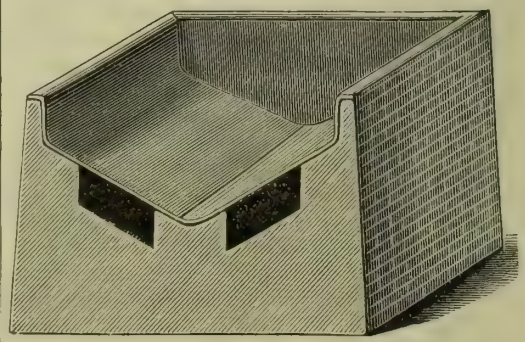


Fig. 22.



bridges are built up within 8 or 12 inches of the sides of the pans, following their sweep, the space

between the bridges being fitted up with brickbats, clinkers, or the like.

In the majority of works the fire gases, after having been used under or over the boiling-down pans, are carried away, as in Plate III., into a flue leading to the chimney, and provided with a damper for the regulation of the draught; but as they possess a considerable degree of heat, it is most advisable, where there is space, to utilize them still further. This can be done in various ways; one which commends itself very much is to conduct the escaping gas over the settlers for "tank-liquor," which must for this purpose be long (say old steam-boilers cut in two) and covered over by an arch; in that case they not only communicate to the settled tank liquor a preparatory heat before it is run into the pans, but they will leave behind with it a great portion of the mechanically carried away particles of liquor and salts from the pans. This does not amount to very much, but it mounts up in the long run to something worth saving. As the settlers for tank liquor are in any case placed in such an elevation as to be able to run into the pans therefrom, there should be no great difficulty about it, especially where the chimney stands on a bank at a higher elevation, which is very usual on the Tyne. The escaping heat may also be used for warming the water used for lixiviating the tanks.

In all cases, even where the fire only heats one boiling-down pan, ball-furnaces require a good draught to work properly, and they are therefore mostly connected with tall chimneys, from 100 feet upwards. The writer succeeded in increasing the output of several ball-furnaces by 50 per cent. by abolishing their chimneys of 40 feet height, one for each furnace, and substituting for them one common chimney of 130 feet height.

The balling operation in the furnace described above is carried on in the following manner:—When the furnace has been heated up sufficiently (which takes at the week-end, after a "damp-up," only five or six hours; but in the case of a "cold heat-up," perhaps twenty-four hours)—viz., to a bright red heat—the charge of sulphate of soda, carbonate of lime, and coals is put into the back bed, either through the working door, or preferably by dropping it in from the top through a hopper. In the regular course of work this charging is done when the ball on the working bed is about half finished; and whilst it is entirely finished, the new charge on the back bed obtains a preparatory heating. After the ball on the working bed has been drawn into the "bogie," the furnace is allowed to go empty for five minutes, or even longer, to heat the front bed thoroughly; and only then the new charge is transferred from the back bed to the working bed, principally by means of an oar-shaped tool, called "slice" in Lancashire, or "paddle" on the Tyne. The paddle head is in this case preferably of cast iron, about 24 inches long, 5 inches wide, and five-eighths of an inch thick. On the Tyne it is very usual to "split" the ball—that is, to move in the first instance only about two-thirds of the ball-mixture from the back bed to the front bed, in order to get more heating surface and easier work whilst the mixture is still rough. The portion brought on to the working bed is well spread out upon it, and moved towards the fire-bridge, where the heat is greatest. It must be well turned over, so as to expose every part of it to the action of the flame, and the "paddle" or "slice" plays here the greatest part still; the parts softened by the action of the fire are turned down, and fresh surfaces are turned up. This turning over has to be repeated about twice; and as soon as the charge begins to soften, the remainder of the mixture is worked down into it from the back bed. In between the turnings-over the working door is let down, and the furnace fire is allowed free action on the charge for several minutes. After the whole has been thoroughly softened, the workman must keep uninterruptedly at the work, because the critical time has come. He must therefore continue turning the mass over and over with the paddle. It becomes in this stage almost liquid all over, but it would be very wrong to draw it just yet; the "paddling" must be continued, and after a few minutes the mass becomes much stiffer. The coal contained in it is now mostly consumed. It is now time to "rake" the ball. The workman, without any interruption, takes down his rake (with cast-iron head), and thoroughly works up the mass, mixing it up as equally as possible, and working it all the time towards the door. His tools, which weigh about half a cwt. each, are supported by the horizontal bars shown in Plate III. in front of the doors. Before using the rake, these bars and the rake-shank are all greased with cart grease. There is besides a chain with a hook at its end hanging down from the rafters in front of the furnace, which enables the furnaceman to rest the fore-end of his tool as well, and materially lightens his actual exertion. Everything now depends upon the judgment of the furnaceman. As soon as he thinks that the ball is quite stiff enough, and before it has had time to go further and to be "burnt," he pulls it, by means of his rake, out into the "bogie" or "pot," which has been beforehand placed in front of the working door. Only just before the raking out, jets of flame, caused by carbonic oxide, and burning with a yellow sodium flame, appear in the mass; these are called "candles" in Lancashire, "pipes" on the Tyne, and they should burst out equally all over the ball while it is being and after it has been drawn, and a practised eye judges from their regular appearance whether the ball has been well made. The latter is well stirred up and mixed in the bogie itself, and ought to swell up and rise in the same; the action seems indeed to go on even then, and to continue till the ball is cooled down. It is allowed to cool and solidify till just before the next ball is ready for the final raking, when the old ball is wheeled away, tilted out of the bogie, and the latter wheeled back to the furnace to receive the new ball.

There is very little difference in the appearances

which the ball presents in the furnace, whether the carbonate of lime has been introduced as chalk or as limestone; it takes about equal time and labour to make a good ball in either case, but there is a decided difference in heat. The furnace must be kept much hotter for chalk than for limestone. Men who are used to chalk are apt to "burn" balls when they have to use limestone, whilst in the opposite case, those used to limestone make "soft" balls when they come to use chalk—both, of course, only till they have accustomed themselves to the new style of work.

Sometimes an arrangement is used by which the fire-damper goes down whenever the working-door is raised; this is to prevent a mechanical carrying away of sulphate by the draught during charging, but such refinement is only rarely practised.

The importance of working the ball-mixture well with the paddle and the rake is well illustrated by some comparative trials made by Kolb on the large scale with a mixture of 106 sulphate, 101 chalk, and 53 coal. The analysis of two balls, one of which (A) was well turned over and worked through, whilst the other (B) was badly worked, showed the following result:—

	A.	B.
Sodium carbonate,	62·20	51·20
Sodium hydrate,	4·72	7·15
Sodium sulphide,	1·12	4·58
Sodium sulphate,	2·06	7·48
Together corresponding to sodium carbonate,	72·2	63·3

The amount of work which is taken out of a furnace varies according to the time the men work. If they work in two shifts during the twenty-four hours, it is usual to make only 12 balls in each shift, or 24 in the twenty-four hours; but if (as is now usual on the Tyne) they work in three shifts of eight hours each, they get 9 balls per shift, or 27 balls in twenty-four hours. A greater number of balls *can* be made, but scarcely of the best quality.

The amount of fuel used varies according to the quality of coals. The writer has made prolonged trials with several descriptions of Durham "manufacturing small," and found the average consumption to vary from 25 to 27 cwts. for each ball-furnace (producing the full work of 27 balls) during 24 hours.

The weight of a well-worked ball should be about 4 cwts. 3 qrs., but it varies to some extent round that figure.

A practical man can easily tell from the appearance of a ball whether it is good or bad; whether it has been too long or too short a time in the furnace; whether it has had enough work or not; whether it is short of limestone (chalk) or coals, or has too much of either. A single glance tells him much more in all these respects than a chemist could make out by a complete analysis, which would only refer, moreover, to a small portion of the ball, and take a very long time indeed. It is hardly possible to convey an idea of what a ball ought to be like by mere description, but a few words may not be out of place upon this subject. A ball ought to be of a blackish-brown colour before it is broken; more particularly should that brown colour (of a lighter shade) appear as a skin on the surface which has been the upper one in the "pot." If a ball is too black, it has either too much coals or, which is more often the case, it has not been fired long enough. When broken, it should appear honeycombed like pumice, not dense, and of as uniform a texture throughout as possible; the colour should be slate-grey, showing small bits of coal in some places, not pinkish. If it appears dense, and not sufficiently honeycombed, it has not been long enough in the furnace, and has not got beyond the stage described above where the mass is nearly liquid; it is then called a "soft" ball, and such black-ash is not only badly decomposed, but difficult to lixiviate, and sure to give a low yield. A whitish colour, generally seen already on the outside, shows excess of carbonate of lime; many large pieces of coal, excess of the same. A pinkish colour testifies of slovenly work; equally so does a rough structure, showing streaks of chalk, of coals, &c., running alongside one another. Sometimes a ball, on breaking up, is found to be of a brick-red colour; oftener, at least parts of a ball are of that colour (spotted). These balls have been "burned," that is, they have been too long in the fire, either from sheer neglect of the workman, or because he wanted to make up by greater heat for deficient work in "paddling." It is usual not to pay the man for such "red" balls, as they contain a very large proportion of caustic and sulphide of sodium, and yield very inferior ash. If a ball were made according to the description given by M. Payen, and in many other books—that is, if it were only drawn when the jets of flame *begin to disappear*, instead of raking it when they *begin to appear*—it would most certainly be a "red" one, and would be condemned. It is also a mistake to assume that a ball becomes less soluble the more it is fired; on the contrary, the balls which are most difficult to lixiviate are those which have not been long enough fired (the "soft" ones). This may be either sheer neglect of the workman, or it may arise from bad draughts or other impediments to the furnace becoming properly heated. Of course, if a ball were left in a *long* time after it was really finished, it might again become less soluble; but it would be so utterly spoiled in that case, that the difficulty of dissolving it would be one of its minor faults. It seems, however, certain that the longer the ball is left in the fire, the more does the sodium pass into the state of compounds absolutely insoluble in water, and totally irrecoverable by the manufacturer.

The eye of an experienced foreman or manager is by far the best judge of the quality of black-ash, and really much more reliable than the analysis in the laboratory, for the simple reason that it can take in the quality of the ball as a whole, while the chemist can only test a small sample; and it is extremely difficult to obtain a sample representing the real average composition of the black-ash even from a single ball, let alone from the hundreds

made daily in any large works. It is usual in most works to test the balls in some way or other, nevertheless—say a sample from each man's work daily. In some cases these samples are tested for their alkalimetrical percentage, for sulphides, and sulphates. This involves a great deal of labour, and gives after all only very uncertain indications, owing to the difficulty of obtaining a really representative sample. A much simpler mode of testing can, however, be resorted to. Whilst the eye readily detects any excess in sulphides, it is more difficult to detect whether any sulphate has been left undecomposed. It is therefore useful to weigh 10 grams. of the sample into a bottle marked for 203 c.c. (of which 3 c.c. correspond to the volume of the insoluble residue), and to shake it up for half an hour with lukewarm water, which can be done with many samples at a time. The solutions are allowed to subside, and 10 c.c. of the clear liquid are taken out of each, supersaturated with pure hydrochloric acid, a little barium chloride added, and the whole diluted to 20 c.c. If the liquid then appears quite clear the ball will be pronounced "good;" if it be slightly opalescent, it is only "indifferent;" and if there be a copious precipitate, it is "bad." This rough test serves as a supplementary aid to the ocular inspection of the balls.

All the above descriptions refer to the ordinary English hand-worked ball-furnace, which is substantially the same on the Tyne, in Lancashire, in Scotland, and in the few other localities in England where alkali works exist. The hand-worked furnace has also lately been introduced into Germany, where it is now more common than the "French furnace." The latter exists in many French alkali works. Its principal difference from the English furnace is its much larger size. It appears that in France the size of ball furnaces has been more and more enlarged. Payen ("Précis de Chimie Industrielle") gives the following table showing this gradual increase in size, at the same time the weight and number of batches, the total work, and the alkalimetrical titre (1 m. = 3·28 feet; 1 kil. = 2·2 lbs. avoirdupois).

	Length of the bed.	Width of the bed.	Surface of the bed.	Charge.		Number of batches in 24 hours.	Weight worked in 24 hours.	Alkalimetrical titre.
				For 1 metre Superficial.	Total.			
	M	M.	M.	Kilos.	Kilos.		Kilos.	
Original furnace of Leblanc and Dizé.....	2·00	1·40	2·80	130	364	5	1820	26 to 30
Payen's furnace,.....	3·00	2·00	5·00	125	725	6	4340*	32 to 35
Darcet's furnace,.....	3·25	2·66	7·00	65	455	12	5244*	33 to 36
Clément's furnace,.....	6·00	2·00	11·00	136	1496	6	8976	35 to 40
" furnace,.....	9·00	3·00	24·00	136	3264	6	19584	

* *Sic;* the calculation gives 4350 and 5460.

In connection with these figures it will be useful to remember that the English ball charge of say 3 cwts. sulphate of soda, 3¼ cwts. of limestone, and 1½ cwt. of coals is equal to 393 kilos. That is little more than the charge in the smallest French furnace; but the large number of twenty-seven charges represents a total weight of 10,611 kilos., or more than Clément's first furnace. The French furnaces have only a working bed, no "back-bed" or "shelf"; and they have far more working doors than the English ones—three or four in the side, one in the end (the "snore holes" running at each side of it), sometimes even two at the opposite side of the furnace.

Payen states as the average size of the charges:—935 kilos. sulphate of soda, 986 of carbonate of lime, 480 small coals, and 145 mother salts (residual from the refining process). Of such charges six are made in twenty-four hours, representing a total of 5610 kilos. sulphate of soda (about equal to 5 tons 10 cwts., or not quite 37 English balls), with an expenditure of 2800 kilos. coals = 2 tons 15 cwts. The work is done by six furnacemen and six assistants, in three shifts, relieving each other every eight hours. The average time in minutes for each stage of the operation is as follows:—30 to charge and spread the batch; 30, 35, and 20 for the 1st, 2nd, and 3rd working through; 20 for the last working and drawing; 105 for the intervals of rest between the workings—altogether 240 minutes. Each batch gives 1525 black-ash (this seems extremely short weight), and shows 38° by the alkalimeter. The raw materials are generally ground altogether, and the balls, being much denser than English ones, are also crushed to small pieces.

It does not appear that the large French furnace has any advantage over the small English furnace. It is very difficult, indeed, to heat the large bed of the French furnace quite equally, and to work the mass in the same into a completely homogeneous batch; there seems also to be great danger both of "burning" the ball, at least partly, and of causing a loss of insoluble soda. On the Continent the supervision of the operation is generally very strict, both by the foremen and the chemists, and the defect of the process may be partly counterbalanced by greater care; and there seems to be besides the less reason for English alkali-makers adopting the French furnace, inasmuch as it undoubtedly requires much more manual labour than the English one. The consumption of coal (the figure given by Payen can hardly be relied upon as decisive) can hardly be less in the French than in the English process. It should be stated that the English form of ball-furnace is now found in many French alkali works.

Revolving Ball-furnace.—The introduction of this apparatus into alkali works marks an important epoch. The furnace was the invention of Elliott and Russell, who patented it in 1853. Owing partly to their incomplete mechanical arrangements, and partly to

the almost insuperable difficulties which their balls offered to lixiviation, their invention remained useless, till Messrs. Stevenson and Williamson, of the Jarrow Chemical Works, South Shields, made very considerable improvements both in the mechanical and in the working details, which were ultimately crowned with perfect success. This was, however, a question of time, and up to a few years ago it might be truly said that, although the revolving ball-furnaces were undoubtedly a success, their advantages over the ordinary hand-worked furnace did not seem so apparent as to warrant their very much higher expense. For the last few years, however, the advantages of the "revolvers" over the hand-furnaces have been preponderating, and they have been made still more apparent by increasing the size and strengthening the working parts; the expense both of working and of repairing the revolvers has also been materially reduced. Three of the largest works on the Tyne, and several in Lancashire, have entirely abolished hand-furnaces and replaced them by revolvers; and many others both on the Tyne and in Lancashire are doing part of their work with them. It seems that in a few years in all but the smallest alkali works there will be no ball-furnaces found except revolving ones. The advantages claimed by the patentees, as follows, seem to be borne out by the facts, viz.:—

1. The whole of the contents of the furnace are heated with such uniformity that no portion ever becomes hot enough to cause a serious loss of soda by volatilization.

2. The atmosphere inside the furnace is always deoxidising, as the furnace never requires to be opened during the mixing and fluxing.

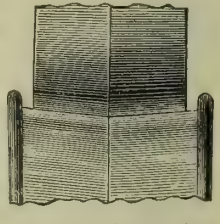
3. As one revolving ball-furnace does the work of several (at first three, now four or five) hand-furnaces, less skilled labour is required to turn out the same quantity of work, and a more complete decomposition of the sulphate of soda is effected by the more perfect mixing of the materials.

4. There is less absorption of soda into the brickwork than in the beds of the ordinary furnaces, and less wear and tear, as no coals are used in the process.

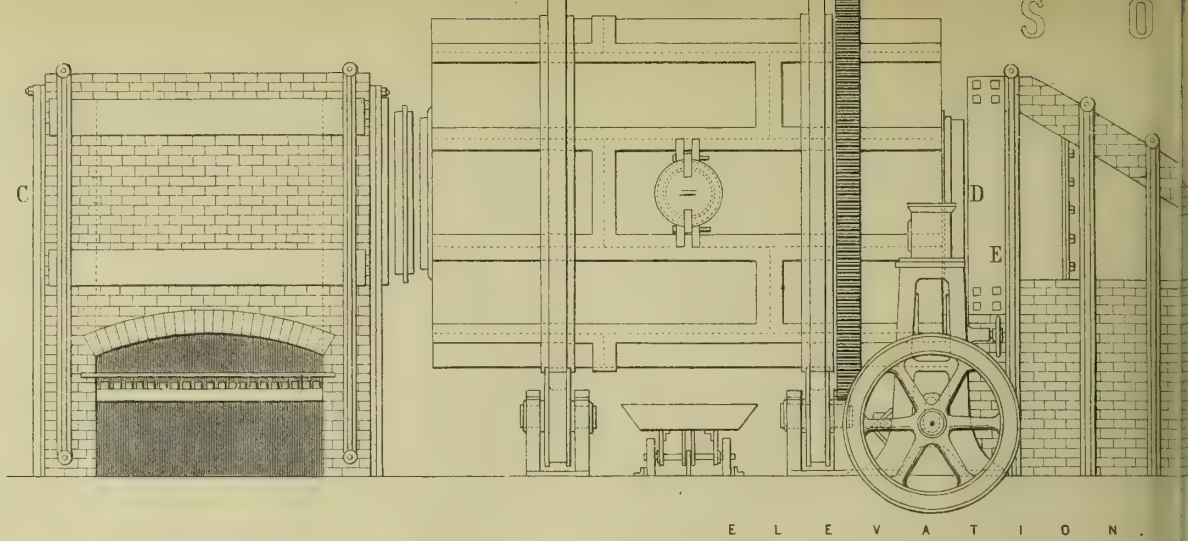
After many years' practical work it is possible to make more positive statements from experience, and to summarize the advantages of the revolvers over the hand-furnaces, thus: less labour (skilled and otherwise), less fuel, stronger ash (because of the better decomposition of the sulphate), fewer repairs. The one drawback urged up to the latest time against the revolvers, viz., smaller yield of ash, has now been overcome so far that it can be said with certainty that their yield of *available sodium carbonate* (and nothing else is paid for by the customers) is considerably *larger* than that of hand-furnaces.

The early plan of revolving furnaces has been completely superseded in everything except the leading fact, that the working part of the furnace consists of a brick-lined cylinder of iron plates. The diagrams given in Plate IV. represent a furnace and pans embodying the latest improvements, as constructed by Messrs. Carrick and Wardale, of Gateshead-on-Tyne, and erected in several alkali works. The revolving furnace proper consists of a cylinder of boiler-plate, half an inch thick, lined with fire-bricks. The wrought-iron shell is 15 feet 6 inches long, and has an inside diameter of 10 feet 2 inches, properly fitted with strips, gussets, and stays. All the seams are broken-jointed, butted, lapped at both sides, and double-rivetted. In each end there is a hole ("eye"), 4 feet in diameter, protected with strong angle irons; and in the circular part of the shell there is a charging hole of 18 inches diameter, with a door. This shell is strengthened by two very strong cast-iron rings, rivetted firmly to it, and hooped with solid cast-steel tyres, 6 inches by 2 inches in section. These steel tyres are accurately turned and shrunk hot on to the cast-iron rings, and firmly secured by a sufficient number of turned tapered bolts. These tyres are afterwards turned to work in Carrick and Wardale's patent "V'd" rollers in the furnaces erected by them. The steel tyres are always in one piece; but the cast-iron hoops are sometimes made in several pieces, whose joints run obliquely across the section of the hoop, the object being to allow of some expansion and contraction without a breakage of the hoop. A large spur wheel, $7\frac{1}{2}$ inches broad, runs round the circumference of the cylinder, and is securely bolted to a carrying ring, and rivetted to the shells. The revolver runs upon four strong carrying wheels or rollers, 3 feet diameter, which are provided with cast-steel tyres, or even made entirely of cast steel. These are accurately bored to receive short shafts, which are keyed into them, and work in carriages, fitted with the proper means of adjusting the cylinder in a perfectly level and true position. Those made by Carrick and Wardale are of cast steel or of drilled cast iron, and called "V'd" rollers, from the shape of their periphery, which resembles a very flat V (Fig. 23). The object of this depression (a quarter of an inch deep), which is ground perfectly true with emery, and to which the steel tyres are perfectly fitted, is to keep the furnace running truly without any side motion. Previous to this, the plain or coned ordinary railway wheel tire was used, which had the disadvantage that the furnace ran from side to side until it was brought up by either flange.

Fig. 23.



The revolver is driven by a vertical steam engine, with inverted cylinder $12\frac{1}{4}$ inches diameter and 14 inches stroke, and so arranged that the speed of the revolver can be varied from about five turns per minute to one turn in five minutes. The engine is fitted with link motion, so that it can be quickly stopped or reversed by levers within easy reach of the platform. It drives directly a spur pinion on a

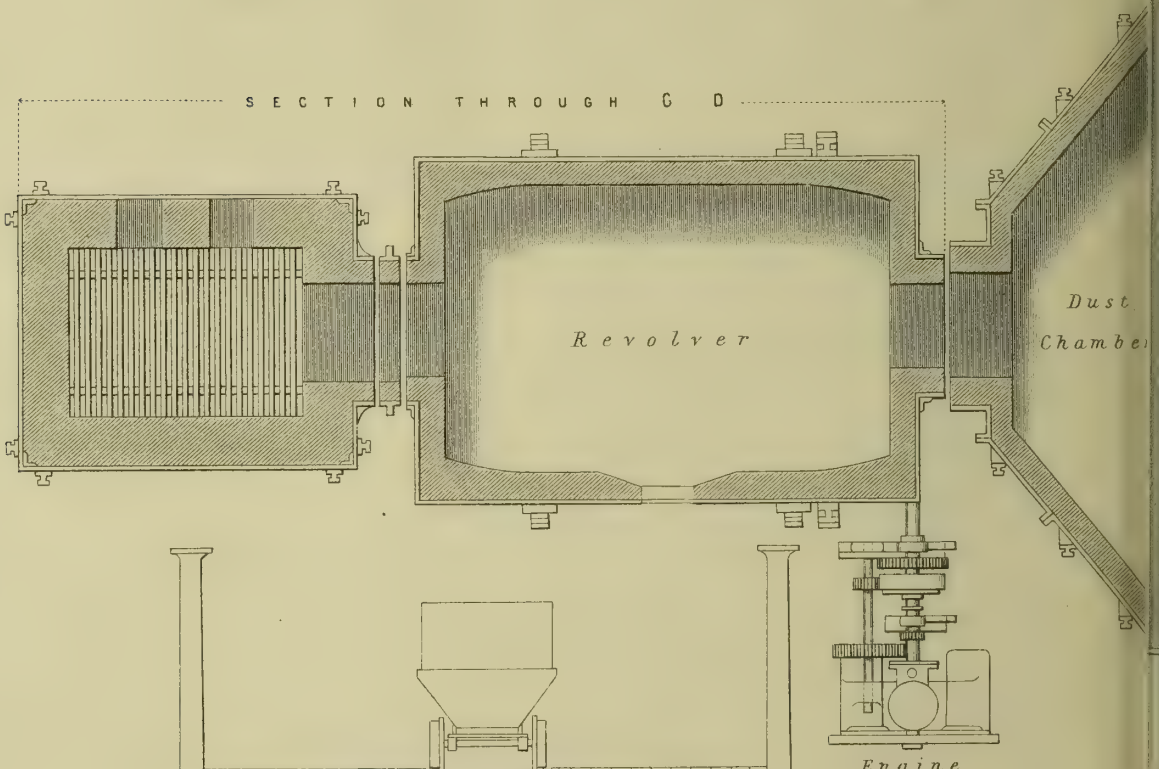


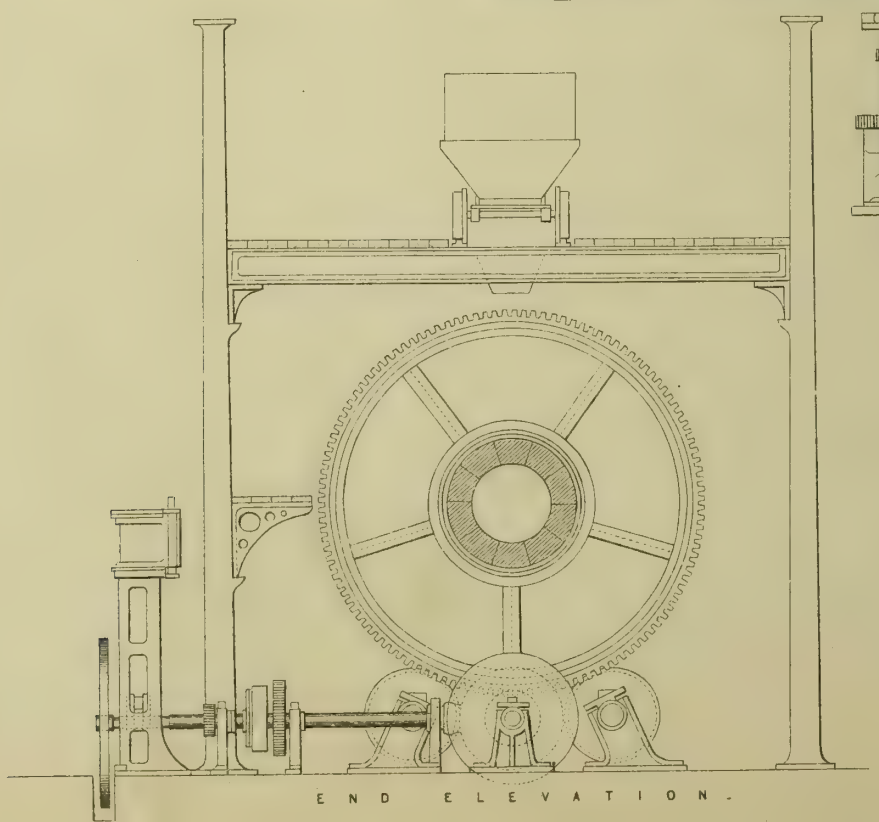
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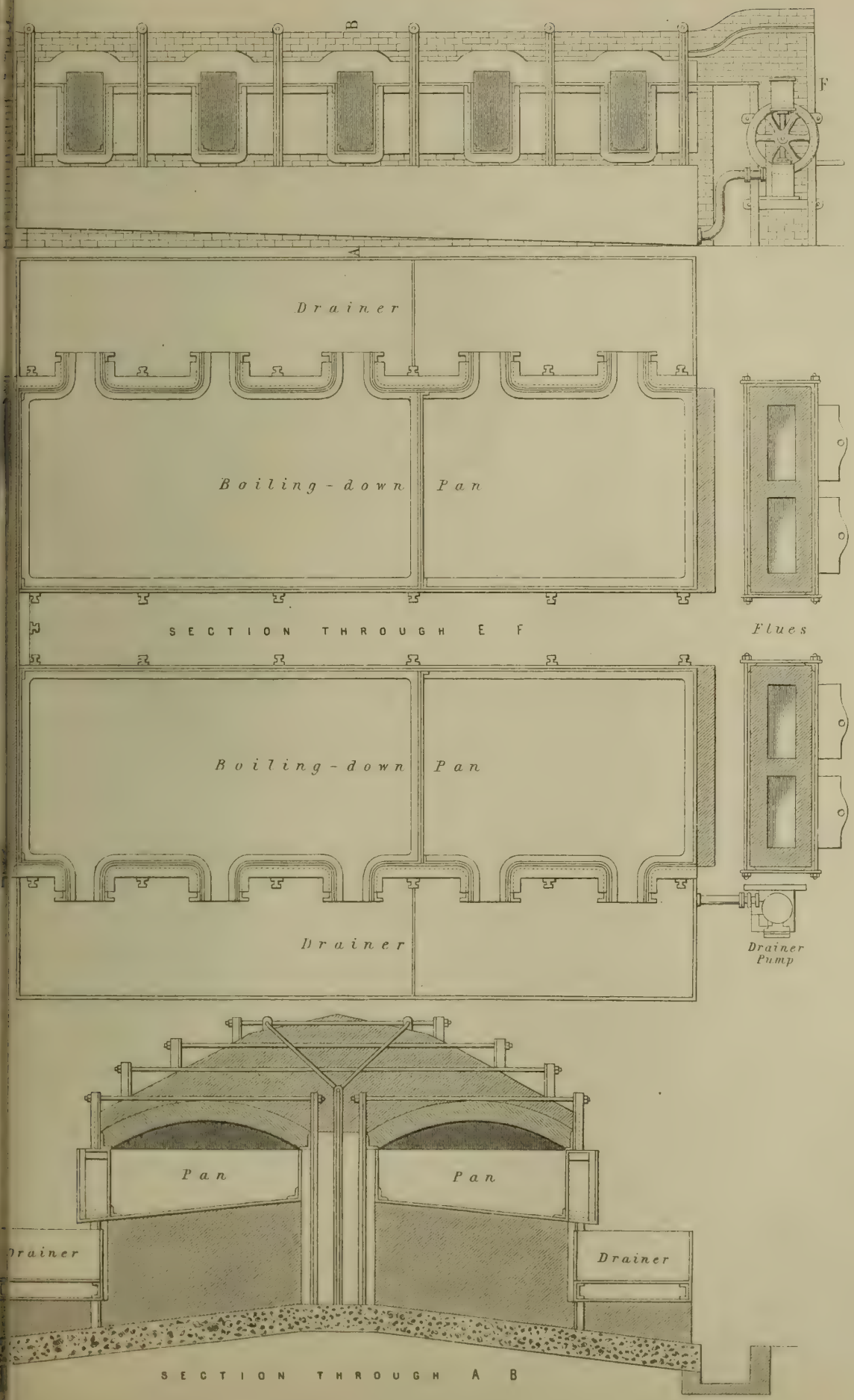
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E N D E L E V A T I O N .

EVOLVING BALL-FURNACE & PANS.



shaft of 5½ inches diameter, which gives the quick motion; the slow motion is produced indirectly by a lower gearing. It is steadied by a fly whele of sufficient weight. The whole is fixed on a set of bed plates, of box-girder form, all bolted together and bolted down upon a solid stone or concrete foundation, so as to form one entire and complete bed.

On one side of this cylinder is the fire-place; on the other side, the dust chamber and the pans. The fire-place is sometimes not provided with grate bars, and serves only to produce a flame from generator gas; but in the great majority of cases direct firing is preferred. In that case the fire-place is about 6 feet to 6 feet 6 inches long (in the same direction as the axis of the cylinder) and about 4 feet 6 inches wide—both inside measurements. The bars run across, from the front to the back, and two stoke holes in the front serve for charging the coals. There is no fire-bridge in the usual sense, but only a hole exactly corresponding to the "eye" in the cylinder. There is a space of about 12 inches between them, which is partly filled by an iron ring lined with fire-brick, and suspended from above; but the air has free access round this ring, so that a constant indraft into the furnace takes place through the eye, and assists the complete combustion of the gas within the revolver. The eye on the other side of the cylinder is so arranged that the man in charge can look into its interior, and observe the state of the charge constantly. From that side the flame passes first into a capacious smoke chamber for the retention of flue-dust, and is then divided in two parts, in order to heat two boiling-down pans running parallel to each other. These are about 28 feet long and 8 feet broad each, with four or five drawing doors and drainers running along their fronts, like those described above in connection with the ordinary ball furnace. Frequently the pans, as well as the drainers, have a partition running across them, and dividing them into a larger and a smaller section. The red liquor is then pumped back exclusively into the smaller section, and the salt drawn out of it gives weak and coloured ash, whilst that from the larger section, which is kept quite free from red liquors, is of very great strength (55 to 56 per cent.) and purity. As the quantity of red liquor is, of course, very large, it is usual to provide a special steam pump for the same. Sometimes the settling pans are fixed on the arches of the boiling-down pans proper, in order to receive some preliminary warming. The flue to the chimney is, as usual, provided with a damper, and it being necessary to have very strong draught at command, as a rule no other flues are allowed to go into the same chimney.

The lining of the revolver proper is barrel-shaped—viz., 9 inches thick at the ends and 4½ inches in the centre. Two horizontal rows of fire-clay lumps ("breakers") project over it, to the extent of 9 inches near the ends and 14 inches at the centre. These serve for mixing the charge thoroughly, and turning it over during the revolution. They act like cascades when the stuff has been liquefied.

It may be of interest for some readers to see what the cost of such an apparatus is; an estimate from the above-mentioned firm runs as follows:—

Revolving furnace, engine, and gearing, erected complete,	£1120
Cement concrete foundations for same,	60
Boiling-down pans,	140
Drainers,	75
Drainer, pump, and pipes,	65
Plates, binders, and bolts,	160
Mason work, including cement concrete flooring,	220
Twelve ball bogies,	54
Three chalk waggons,	43
	£1937

To this must be added the cost of the overhead railway, of the elevator for the materials, and of sulphate crushers, where the latter are used.

Much larger revolvers, built in a barrel shape, are now being erected at Glasgow.

Each revolver must necessarily have its own driving steam-engine, as it is imperative to have it entirely under control, so as to drive it slow or fast, stop it and reverse it at a moment's notice, without being hampered by any other work attached to the engine. One single engine, however, suffices for the purpose of crushing the sulphate for several revolvers (which is in some works avoided by merely screening it), and for elevating the materials to the railway running over the revolvers. Generally, the sulphate, chalk, and coals are each filled into conical waggons holding a full charge, about 5 feet × 4 feet × 4 feet 6 inches; these are constructed so as to empty their contents at once through a hopper into the charging hole of the revolver by drawing a bolt which holds up their bottoms. The charges are not the same in every works, as the size of the furnace and the nature of the material varies.

For the size of furnace described, and when using chalk, the charge is as follows:—30 cwts. of sulphate, 33 to 35 cwts. of chalk, and 17 to 19 cwts. of coals, according to quality. The sulphate must either be crushed, or, which is the cheaper course, it is thrown through a screen with half-inch meshes, and only the lumps are broken. The chalk is used without crushing or drying, this being unnecessary, as, when the damp chalk is tipped into the bright red-hot revolver, the moisture is almost instantaneously converted into steam, and causes the lumps of chalk to fly into fine powder with the force of a small explosion. The coal is divided: two-thirds are charged with the chalk and one-third subsequently with the sulphate. The mixture of a Lancashire work is stated: 30 sulphate, 27 limestone, 17 coal.

First of all, the chalk is tipped into the revolver (whose charging hole has, of course, been brought straight under the hopper), and two-thirds of the coal, as before mentioned. The engine is then started, and the slow motion is used, say one turn in five minutes. After an hour and ten or fifteen minutes the stage of "liming" is reached; that is, a certain portion of the chalk has now been causticized. The exact appreciation of this moment is the principal object of the revolver-man, who sits opposite

to the chimney-end of the revolver, and observes through the "eye." A bluish flame round the same is one of the marks of that stage being reached. The object of "liming" (which formed one of the principal improvements introduced by Messrs. Stevenson and Williamson) is this: to cause the revolver-balls, which are extremely dense and difficult to lixiviate, to burst in the tank by the slaking of the caustic lime, and thus to open them sufficiently for a thorough lixiviation.

James Mactear, of St. Rollox, Glasgow, has introduced an improvement which is to do away with the tedious operation of liming. It consists in dropping in the total mixture of sulphate of soda, limestone, and coal at one time, the quantities of the latter being smaller than usual in ordinary revolvers; then, after the decomposition is complete, adding a small quantity of caustic lime (say 5 per cent. of the sulphate), and quickly mixing it up with the charge by rapid revolutions of the cylinder; the charge is then at once drawn. The advantages of Mactear's process consist in a saving of lime (in both forms), in a large increase of production from a given size of plant, and less caustic soda in the liquors, whilst the balls dissolve precisely as well as any other balls, and have quite as little soda in the waste (as low as 1·3 per cent. Na_2O). As the total amount of "waste" is smaller than in ordinary works, the absolute loss of soda in it is also correspondingly less. This process, which seems to be a very great improvement, has been recently carried out quite successfully.

In most works the usual way is still to "lime" the balls as above described. When the "liming" has taken place the revolver is stopped, the sulphate and the remaining third of the coal are tipped in, and the engine is started again with the slow motion. It will be observed that the proportion of mixing coals is larger than in the hand-furnaces; this excess of mixing coal serves partly for a more complete decomposition of the sulphate, and partly to make the balls more porous. During the charging of the sulphate the damper is let down to avoid any stuff being carried away by the draught; but it is raised again after ten minutes. About twenty minutes afterwards the appearance of a bright yellow flame round the working hole shows that the sulphate is now melted, and the slow motion is now changed for the quick one, say two revolutions per minute. The revolution is then continued till the workman judges from the appearance of the charge that it is time to finish. The consistency and colour of the charges, and the bright yellow flames ("pipes") darting especially from those parts adhering to the "breakers," offer the necessary data for his judgment. This last stage takes about half an hour. The engine is now allowed to run at full speed for two or three revolutions, so as to gather up the ball; the charging door is hooked on to a pulley and chain and taken off, and on turning round slowly the liquid ball runs into the bogies, of which a sufficient number (ten or twelve), connected by a bar of iron, have been ranged underneath on a tramway, and which are slowly drawn away, by means of a winch, as they fill. The bogies are 4 feet by 3 feet wide at the top, somewhat narrower at the bottom, and 10 inches deep, and their projecting tops nearly touch one another as they stand in the row. Nine of them are generally filled at once, and by quickly turning the revolver round enough is gathered to fill another two or three bogies.

Including the necessary pauses for stoppages, the average time for finishing a revolver charge is not quite two and a half hours (in Mactear's process much less). Generally ten charges are finished in twenty-four hours, equal to 15 tons sulphate of soda, or 90 tons per week of six days. Some state that they work as much as 115 tons per week; but the above statement is authentic. Two men by day, and as many by night, do all the work about the furnace, one of whom is only a common labourer. The saving in wages against ordinary furnaces thus amounts to 1*s.* to 1*s.* 3*d.* per ton sulphate. There is undoubtedly an advantage in requiring only one-fourth of the skilled labour usual with hand-furnaces, and in dispensing altogether with the gross manual labour of working the balls by hand tools.

The fire-brick lining of the revolver lasts about four months, and takes a week for its renewal.

The consumption of fuel is always stated to be less in revolvers than in hand furnaces for the same quantity of sulphate balled; the saving is differently stated from a quarter to a third of the total.

The appearance of revolver balls is very different from that of hand-made balls. They show, directly after drawing, the "candles" or "pipes" equally well; but instead of a swelling porous mass, they are dense, and become very hard on cooling. If it were not for the "liming" they would not be dissolved at all, and even as it is, they require much more energetic treatment (especially steaming) than hand-balls. Until recently it was assumed that the yield of ash from a given quantity of sulphate was less in revolvers than in hand furnaces; but manufacturers have learned the manipulations better, and nowadays the yield from revolvers, even if it be slightly less in the gross, exceeds that from hand furnaces decisively when the available alkali in the soda ash is considered.

For the reasons stated—saving in labour, saving in coals, and superior strength of the soda ash—the preference is now given to revolving ball furnaces in all alkali works large enough to use the same, in spite of the considerable first cost of the revolvers in comparison to the hand furnaces.

Theory of the Reactions in the Ball Furnace.—The action which takes place when a mixture of sodium sulphate, calcium carbonate, and coal is exposed to heat, as well as the reactions ensuing when the resulting "black-ash" is treated with water, are evidently of a complicated character, and have been very differently interpreted by different chemists. Dumas supposed that, in the first place, the sodium sulphate and calcium carbonate react upon each other, producing sodium carbonate and calcium sulphate:—

$$Na_2SO_4 + CaCO_3 = Na_2CO_3 + CaSO_4;$$

that the calcium sulphate is reduced by the coal to calcium sulphide, with the evolution of carbonic oxide; and that the calcium sulphide joins with calcium oxide to form a compound insoluble in water, of the formula CaO,2CaS. This theory, at least the latter part of it, is based on the assumption that CaS is soluble in water, and that, if it existed as such in black ash, it would, during the lixiviation, decompose the sodium carbonate, thus—

$$CaS + Na_2CO_3 = Na_2S + CaCO_3.$$

This assumption seems, however, never to have been verified experimentally by Dumas or any one else. Dumas expresses the final results of the fusion in the ball furnace thus (converted into the new notation)—

$$2Na_2SO_4 + 3CaCO_3 + 9C = 2Na_2CO_3 + CaO,2CaS + 10CO.$$

The proportions of material corresponding to this equation are, theoretically—

Sodium sulphate,	100
Calcium carbonate,	105·6
Carbon,	38

Considering, in the first place, the impurity of the commercial articles used in actual work, and secondly, the fact that a portion of the coal is sure to be burnt before having done its work, these proportions very fairly agree with the mixtures actually in use in alkali works.

This theory seems simple enough, and it was adopted by Brown and by Unger in its essential features, although they differed in some particulars from Dumas' opinions. But the whole theory was combated by Kynaston (on the strength of researches made in Dr. Muspratt's laboratory), by Gossage, and by Scheurer-Kestner, on the following grounds:—Pure calcium protosulphide, made by igniting gypsum with charcoal protected against access of air, is in itself insoluble in water, and is also very little acted upon by a solution of sodium carbonate. Furthermore, it is a well-known fact that the solution of black-ash always contains a certain quantity of caustic soda. It is certain that no caustic soda exists pre-formed in the black-ash, for the latter would yield it on treatment with alcohol, which, however, dissolves little or no caustic soda from it. It is therefore generally admitted that the caustic soda is only formed during the lixiviation, by the action of the sodium carbonate upon the insoluble part of the black-ash ("tank waste").

If this were essentially CaO,2CaS, it must be expected that the action of sodium carbonate would produce sodium sulphide in the following proportions of two equivalents to one of sodium hydrate—

$$3Na_2CO_3 + CaO,2CaS + H_2O = 2NaOH + 2Na_2S + 3CaCO_3.$$

It is, however, not the case that anything like this proportion of Na_2S is formed in the tank liquor, and the above named chemists therefore assume that Dumas' calcium oxysulphide does not exist, but that it must be considered as a mixture of calcium sulphide and oxide, the latter causing the formation of a certain quantity of sodium hydrate (caustic soda) by its action on the sodium carbonate. Gossage has, furthermore, adduced this very forcible argument against Dumas' views:—That these views require, of necessity, the presence of three equivalents of calcium carbonate for two of sodium sulphate in the ball-mixture, but that he, as well as two other practical alkali-makers, have worked, both on the small and on the large scale, with *equal* equivalents of each, and have obtained real black-ash. He does not deny that the extra chalk is useful, or even necessary for proper work, but only because it affords a larger amount of surface for reaction; and thus expedites the fluxing reaction, and thereby prevents the formation of calcium polysulphide. The opinion of Gossage has been entirely borne out by the success of Mactear's mode of working revolving ball-furnaces, since in this only the real equivalents of calcium carbonate is used.

The calcium oxysulphide found a new advocate in E. Kopp, who based his views on many analyses of soda waste, in which the proportion between CaO and CaS had always been nearly that required by Dumas' formula. The constancy of this proportion was contradicted by Scheurer-Kestner, but Kopp urged again that the soda waste does not form with a solution of sodium carbonate either as much sodium hydrate or sulphate as if CaO and CaS occurred free in it; that the soda waste does not, like free lime, precipitate MnO_2H_2 from a solution of $MnCl_2$; and that an artificial mixture of 2CaS and 1CaO forms a mass which does not react either on sodium carbonate or on manganese chloride, thus behaving like real soda waste.

The question was further inquired into (1864–66) by Scheurer-Kestner, J. Kolb, Pelouze, Th. Petersen, and Dubrunfaut, all of whom declared against Dumas' theory. Their researches established the following facts beyond any doubt:—1. Calcium protosulphide is *very* slightly soluble in water (1000 parts of water dissolve at the ordinary temperature only 0·08 CaS, according to Scheurer-Kestner; 0·23 according to Kolb; 1 to 1·5 according to Pelouze), and it is extremely slowly decomposed by a solution of sodium carbonate. 2. There is certainly neither Na_2O nor NaHO in black-ash, for alcohol extracts nothing, even after the mass has been moistened with water. 3. When black-ash is gradually lixiviated, the percentage of the solution in sodium sulphate does not increase *pari passu* with that of sodium hydrate; but at a very much slower rate. 4. If equal quantities of black-ash are treated, *a* with milk-warm water, *b* with boiling water, there are in both solutions equal quantities of sodium hydrate, but in the latter also a large quantity of sodium sulphide and less sodium carbonate (Pelouze). 5. If soda waste after lixiviation is treated with a strong acid, the expelled quantity of H_2S and CO_2 is sufficient to saturate the calcium completely; but this would be impossible if there existed in it a large quantity of CaO,2CaS, and if the caustic soda

could only be formed by a small excess of caustic lime existing alongside of it.

Kolb tested the question in a different manner, viz.—on a large scale. He composed two mixtures, one corresponding to Dumas' equation, but with the excess of coal necessary in practical furnace work, thus:—

I. $2Na_2SO_4 + 3CaCO_3 + 12C = 2Na_2CO_3 + CaO,2CaS + 10CO + 3C.$

The other corresponding to a formula proposed by Dubrunfaut, and supposing only CaS, viz.:—

II. $3Na_2SO_4 + 3CaCO_3 + 12C = 3Na_2CO_3 + 3CaS + 12CO.$

If, however, the reaction does not consist in the formation of CaS but of CaO,2CaS, according to Dumas, Kolb's second mixture could only give the following results, as Landolt has shown:—

II.*a*. $3Na_2SO_4 + 3CaCO_3 + 12C = 2Na_2CO_3 + Na_2S + CaO2CaS + 12CO + CO_2.$

That is to say, only two-thirds of the sodium sulphate employed are converted into carbonate, and one-third into sulphide. The two mixtures were furnaced in a ball-furnace under exactly equal conditions, and lixiviated in the same manner. The analysis of the liquors showed that the following products had been formed from 100 parts of sodium sulphate:—

Mixture.	I. $2Na_2SO_4 + 3CaCO_3$.		II. $3Na_2SO_4 + 3CaCO_3$.	
Na_2CO_3	52·60	= 67·0 Na_2CO_3.	59·51	= 65·3 Na_2CO_3.
Na_2O	8·45		3·39	
Na_2S	0·15		2·16	
Na_2SO_4	0·93		6·71	

This shows that the quantity of sodium carbonate formed was equal in both cases; there was in the second case only 2·16 Na_2S formed against 18·3 required by equation II.*a*., and the decomposition must, therefore, have taken place according to equation II. The mixture I. yields a surplus of free lime, which explains the larger percentage of Na_2O in the liquors.

Kolb's experiments, which, it will be observed, agree with Gossage's statements, have never been refuted, and since that time (1866) it has been generally assumed that black-ash does not contain a calcium oxysulphide; but that it must be considered as essentially a mixture of sodium carbonate, calcium sulphide, and free lime.

Dumas' view of the process which takes place in the furnace itself has also been opposed. Dumas' very simple equations quoted above were soon recognized as untenable, the process being decidedly more complicated; but Unger, Brown, Gossage, and Dubrunfaut, who each suggested a different formula, agreed with Dumas in assuming that the coal is converted entirely into CO. Scheurer-Kestner found (1864) that Na_2S and $CaCO_3$ ignited together entirely decompose each other; he also found (like Unger) that on heating sodium sulphate and coal in a retort no CO, but merely CO_2, is evolved, whichever of the two ingredients may be in excess. On the other hand, when chalk and coal were ignited together CO was largely formed (88 per cent. CO against 12 per cent. CO_2); but the decomposition requires a much higher temperature than the reduction of sodium sulphate. On this Scheurer-Kestner bases the following statement of the process in the ball-furnace, in which the three equations *a b c* are supposed to occur consecutively, and *d* to express the sum total of all:—

a. $5Na_2SO_4 + 10C = 5\ Na_2S + 10CO_2.$
b. $5Na_2S + 5CaCO_3 = 5Na_2CO_3 + 5CaS.$
c. $2CaCO_3 + 2C = 2CaO + 4CO.$
d. $5Na_2SO_4 + 7CaCO_3 + 12C = 5Na_2CO_3 + 5CaS + 2CaO + 10CO_2 + 4CO.$

This theory assumes that all the CO_2 required for the formation of sodium carbonate is furnished by the chalk.

Kolb based his view, different from the above, on the following experiments (1866):—Two retorts, one containing a mixture of sodium sulphate and coal, the other chalk and coal, were exposed in the same furnace to a gradually increasing temperature. At a low red heat there was given off, almost exactly at the same time, CO_2 from the first and CO from the second retort. Pure chalk, contained in a third retort, gave off CO_2 when bright red heat had been reached. When a mixture of $Na_2SO_4 + CaCO_3 + 3C$ was heated, a mixture of CO_2 and CO was evolved, showing that the coal acted contemporaneously on both bodies. If therefore the chalk loses its CO_2 at the same time whilst the sulphate is being reduced to sulphide, the reaction, $Na_2S + CaCO_3 = Na_2CO_3 + CaS$, becomes impossible, and it must be indifferent whether calcium carbonate, quick lime, or hydrated lime is used for the soda mixture. Kolb tested this on a large scale, and found it entirely borne out by the facts. He concluded that the CO_2 of the Na_2CO_3 must be furnished either by the reduction of Na_2SO_4 with C, or by the gases of the fire. He tried to decide between these two, by igniting a normal soda mixture in covered crucibles, and he found that this did not yield a good black ash; he therefore concluded that the CO_2 of the fire gas is absolutely necessary for the formation of good black ash, and thus explained the importance of thorough "paddling" and "raking" in the furnace. His theory is embodied in the following equations:—

a. $Na_2SO_4 + 2C = Na_2S + 2CO_2.$
b. $CaCO_3 + C = CaO + 2CO.$
c. $Na_2S + CaO + CO_2 = Na_2CO_3 + CaS.$

In *c* the CO_2 is supposed to be furnished by the fire gas.

This theory was opposed by Scheurer-Kestner (1867), who, like Kynaston and even Leblanc himself, found that altogether normal black ash can be obtained by heating the mixture in closed crucibles. He also found that this reaction took place before a mixture of chalk and coal or pure chalk were decomposed under exactly similar conditions. The CO_2 must therefore be furnished by the chalk.

or, when caustic lime is used, by the reduction of Na_2SO_4 with C. Scheurer-Kestner's explanation of the reaction in the ball-furnace, which is the latest, but will hardly be the last, is as follows:—The materials in the ball-furnace are always forming a mass of a certain depth on the bed. The reduction begins in the upper layers which are mostly heated; Na_2S and some CaO are formed. By turning over the mass, the mass is again carbonated by the CO_2 arising from the reaction of Na_2SO_4 in the lower layers. As the Na_2S fuses, it penetrates the calcium carbonate, and sodium carbonate and calcium sulphide are formed. When the reduction of the sulphate has been finished, and the evolution of CO_2 ceases, the temperature of the mass rises, and then only the chalk present in excess is reduced by the coal, and CO is formed. The arising of flames of that gas is a sign of the end of the reaction.

Composition of Black Ash.—The following table of analyses made by different chemists gives a good idea of how little use a complete analysis of black ash is for practical manufacturing purposes. This product is not only of a most complex character, but its analysis is exceedingly difficult; and the result, even of the same black ash and in the hands of the same chemist, will vary very much indeed, according to whether he has used quite fresh black ash, or the same exposed to air; whether he has washed it with cold, lukewarm, or boiling water; whether the solution has been allowed to stand for some time over the residue or not, &c. Some of the analyses seem particularly suspicious — such as Unger's No. 2 and Richardson's—on account of the large quantity of sodium hydrate, whose presence is denied by the best observers; Danson quotes similarly sodium oxide; and not one of the analyses of black ash found in text books gives any statement of that portion of the soda which is known to exist in *every* black ash in a form insoluble in water, whether it be as sodic-ferric sulphide, or as sodic-calcic-aluminic silicates, or in any other. This makes the close approximation of most analyses to 100·00 quite futile, and proves it to be merely apparent. Stohmann, for instance, whose analyses add up to 100·93, 100·00, and 100·26 respectively, and who does not in them mention soda in *any* other form but that of sulphate, chloride, carbonate, and (once) of hydrate—all of which certainly are soluble in water—yet states further on that of 100 parts sodium sulphate, 3·2 to 5·42 are only recovered in that portion of the black ash insoluble in water; but in what shape his analyses do not show, and they cannot therefore be considered as reliable.

ANALYSES OF BLACK ASH.

	By Unger, from Ringkuhl.		By Brown, from Newcastle.	By Richardson, from Newcastle.	By Murphy (Lancashire).	By Kynaston (Liverpool).	By Danson, Muspratt's Works.	By Stohmann, from Jarrow.		
								Ordinary Furnaces.		Revolver.
	1.	2.						1.	2.	
Sodium sulphate,	—	1·99	1·160	3·64	·748	·395	·8	1·54	1·54	1·06
" sulphide,	—	—	1·130	—	—	—	·4	—	—	—
" chloride,	·4	2·54	1·913	·60	1·308	2·528	3·1	1·42	1·75	1·48
" carbonate,	37·8	23·57	35·640	9·89	41·489	36·879	28·9	44·41	38·45	43·27
" silicate,	—	—	—	—	1·162	1·182	—	—	—	—
" hydrate,	—	11·12	—	25·64	—	—	—	—	3·17	—
" oxide,	1·6	—	·609	—	—	—	8·2	—	—	—
" aluminate,	—	—	2·350	—	·392	·689	—	—	—	—
Calcium carbonate,	—	12·90	—	15·67	·857	3·315	14·2	3·20	—	7·52
" oxysulphide, CaO,3CaS	40·0	34·76	29·172	35·57	—	—	—	38·98	36·91	25·48
" sulphite,	—	—	—	—	—	2·178	—	—	—	—
" hyposulphite,	—	—	—	—	—	1·152	—	—	—	—
" sulphide,	—	—	—	—	33·193	28·681	25·8	—	—	9·38
" bisulphide,	—	—	—	—	—	·435	—	—	—	—
Lime,	8·5	—	6·301	—	9·320	9·270	9·2	0·33	·61	—
Magnesia,	·8	—	—	—	—	·254		0·10	·51	·19
Magnesium sulphate,	—	—	3·744	—	—	—	—	—	—	—
" silicate,	—	4·74	—	·88	—	—	—	—	—	—
Alumina,	1·2	—	—	—	1·020	1·132	6·2	0·79	—	·72
Water,	—	2·10	·700	2·17	—	·219		—	6·71	—
Iron peroxide,	—	—	—	—	3·020	2·658		1·75	2·40	1·48
" sulphide,	1·2	2·45	4·917	1·22	—	·371	—	—	—	—
Silica,	5·0	—	—	—	—	—	2·0	0·89	1·36	1·74
Sand,	—	2·02	4·285	·44	2·259	·901	—	2·20	1·16	2·66
Carbon,	2·6	1·59	7·998	4·28	4·724	7·007	—	5·32	5·43	5·28
Ultramarine,	—	—	·295	—	—	·959	—	—	—	—
	99·1	99·78	100·214	100·00	99·492	100·205	89·8	100·93	100·00	100·26

Black ash may be considered as essentially a mixture of sodium carbonate, calcium sulphide, oxide, and carbonate; all other matters being unessential, although to some extent unavoidable admixtures, carried into the mixture partly by the impurities of the raw materials, partly by the wear and tear of the furnaces and tools. Apart from those matters mentioned in the above analyses, black-ash generally contains very small proportions of ammoniacal and of cyanogen compounds (although most probably *not* as ferrocyanides), and sometimes rarer elements, of which Unger has found the following — titanium, copper, molybdenum, phosphorus, tantalium, fluorine, barium, nickel, cobalt, manganese, lead. Rammelsberg has found vanadium.

The following analyses by G. E. Davies are all free from the above-mentioned faults, and account

for the insoluble soda, which he assumes to be all in the state of a double silicate of sodium and aluminium. The black ash was made with Buxton limestone. A and B are good samples, C was a "red" or "burnt" ball.

	A.	B.	C.	
Sodium carbonate,	28·144	31·807	28·236	Soluble.
" oxide,	5·860	5·614	3·844	Soluble.
" chloride,	2·808	2·574	3·101	Soluble.
" sulphate,	0·192	0·190	3·037	Soluble.
" sulphite,	0·151	0·072	none.	Soluble.
" hyposulphite,	0·189	0·853	0·126	Soluble.
" sulphide,	0·358	0·163	6·645	Soluble.
" aluminate,	0·344	0·752	0·923	Soluble.
" silicate,	1·026	0·914	0·758	Soluble.
" cyanide,	0·186	0·043	0·422	Soluble.
" sulphocyanide,	0·074	0·021	0·077	Soluble.
Calcium sulphide,	29·504	28·744	33·245	Insoluble.
" carbonate,	12·657	9·272	6·087	Insoluble.
" oxide,	10·048	9·488	3·465	Insoluble.
Iron sulphide,	0·554	0·774	1·355	Insoluble.
Alumina,	0·172	1·042	0·624	Insoluble.
Silica,	1·095	0·923	0·973	Insoluble.
Magnesia,	0·266	0·322	0·146	Insoluble.
Soda,	0·344	0·546	0·577	Insoluble.
Carbon,	4·263	4·483	4·958	Insoluble.
Sand,	1·237	0·875	0·842	Insoluble.
	99·472	99·472	99·641	
Soluble iron sulphide,	—	—	0·105	

The analyses given in the above tables represent the silica as combined with one or two of the bases only; this is, however, merely an assumption on the part of the chemists who made the analyses. It is well known that at least a portion of the silica exists as a compound with aluminium, calcium, magnesium, and sodium, which is insoluble in water, but soluble in acids. The totally unavoidable formation of this compound is just the cause of the loss of soda in the "tank-waste." Another portion of the silica exists as soluble sodium silicate, which forms a constituent of every soda ash.

Black-ash is only very slowly changed by lying in dry air at ordinary temperature. Kolb allowed a sample made with special care to cool, protected from the air, and lixiviated one part of it at once, the other after having exposed it for the space of two months to air free from moisture and carbonic acid. Of the latter one portion was left thus at the ordinary temperature, the other at 100° C., and both were ultimately treated just like the first sample. The result was that the two last samples showed a little more caustic; but on the whole about as much available alkali as the first. Dry air at 100° C. only causes a slight increase of weight, but no injurious decomposition. If, however, the heat is increased to 200° or 300° C., and still more, up to a red heat, the colour of the black-ash changes to brown red, and its percentage of available alkali decreases quickly; indeed, it may be reduced to one-half in a very short time. The conclusion is that the cooling of the black-ash after coming out of the furnace ought to be hastened as much as possible; and that, if possible, it ought to take place in closed boxes, as the cause of the loss is practically the oxidation of the calcium sulphide to sulphate, which on lixiviation decomposes an equivalent quantity of sodium carbonate and reconverts it into sulphate. In practice nothing more is done than to allow one ball to cool in the "pot" till it is about time to draw the next one, say three-quarters of an hour; it is then tipped, but not broken up till it is cool.

The above experiments only referred to air free from moisture and carbonic acid. In the ordinary air containing both these the matter is different. In the first instance the caustic lime attracts moisture, and in being slaked to hydrate increases its volume, which makes the balls burst and fall to powder. The calcium hydrate gradually changes into carbonate, the sodium sulphide into hyposulphite. Neither of these changes would be injurious, but the moist air acts at the same time upon the calcium sulphide, and converts it to a certain extent into soluble polysulphides, hyposulphite, sulphite, and ultimately sulphate. On lixiviation all these react upon the sodium carbonate and destroy it, so that the alkalimetrical test of black-ash, even allowing for the increase of weight, goes back continually by exposure to the weather. Erdmann found in a sample of black-ash, originally containing 29 per cent. of sodium carbonate, only traces of that salt after twenty-seven years' lying in the air. The conclusion is that the proper way of treating black-ash is this—to submit it to lixiviation as soon as it has sufficiently cooled, for which forty-eight hours is quite sufficient. Thus the heat retained by the balls is also utilized in the lixiviating process, and it is practically found of great advantage to work up the balls after no longer exposure than two or three days.

Lixiviation of the Black-ash.—The object of the alkali manufacturer is to obtain as much and as pure sodium carbonate as possible from his raw materials, and consequently from the black-ash. The only available means for doing this is to submit the black ash to lixiviation, that is, to separate the soluble from the insoluble portion; the former being further worked up for soda ash, the latter being removed from the factory as "tank waste" (in some cases after first submitting it to a process for recovering a portion of the sulphur from it). The product of the lixiviation varies very much, indeed, quite apart from any variation in the quality of the balls, according to the way in which the process is carried on. Three objects have always to be kept steadily in view, viz.:—1st, To obtain all sodium compounds from the black-ash as completely as possible; 2nd, To obtain them as much as possible in the form of sodium carbonate; 3rd, To obtain a solution as much concentrated as practicable.

The success of these operations depends very much, indeed, upon the manner in which the lixiviation is carried on; but it will be better understood if it is first explained in what manner water acts upon black-ash. It has been mentioned before that black-ash in itself does not contain any sodium hydrate or sulphide, except in very minute quantities, since alcohol, which would dissolve them, practically does not act upon black-ash at all. On the other hand, it is quite impossible to make a solution

of black ash free from either sodium hydrate or sulphide. It is thus clear that both these compounds are formed by the treatment with water, and it is well known that they are formed in very varying proportions, according to the variation in the conditions of the water treatment. It may be taken as a general thing that the alkali manufacturer wants to avoid the operation of both sodium hydrate and sulphide during the lixiviation as much as possible, and it thus becomes of great importance to fix the conditions under which their formation is either favoured or impeded. The most exhaustive experiments upon this matter have been made by Kolb, and the following table summarizes his results:—

100 Grams. Black-ash treated with: c.c. Yielded—	Water.	6 Hours at			24 Hours at			1 Week at		
		15° C.	40° C.	60° C.	15° C.	40° C.	60° C.	15° C.	40° C.	60° C.
Grams.										
Na_2CO_3,	350	—	—	—	34·7	31·4	31·5	31·5	25·8	26·4
Na_2O,		—	—	—	5·7	7·8	7·6	7·6	9·5	7·2
Na_2S,		—	—	—	trace.	·2	·3	trace.	2·2	3·7
Na_2CO_3,	500	38·5	37·4	31·5	38·6	35·4	26·8	37·0	34·2	25·5
Na_2O,		3·3	3·9	6·8	3·3	5·1	6·7	4·2	5·7	6·6
Na_2S,		·2	·3	·7	·3	·4	4·7	·3	·4	5·9
Na_2CO_3,	1000	40·2	35·9	34·2	38·6	34·2	31·1	35·2	31·4	23·2
Na_2O,		2·3	4·4	5·4	3·3	6·0	6·6	5·0	6·3	6·0
Na_2S,		·3	·5	·8	·3	·8	2·0	·3	·8	7·8
Na_2CO_3,	2000	38·2	36·1	37 9	37·6	34·7	33·1	34·5	31·5	19·5
Na_2O,		3·3	4·7	3 3	3·8	5·9	6·2	5·3	6·3	6·3
Na_2S,		·2	·5	·6	·4	·5	1·0	·5	1·5	10·2

This table leads to the following conclusions:— 1. The quantity of sodium hydrate formed is not influenced very much by the quantity of water, but it increases with the time taken up and the temperature employed. The difference between 40° and 60° C. (104° and 140° Fahr.) is, however, not very essential. 2. Sodium sulphide is hardly more influenced by the quantity of water, it also increases with the time and the temperature, but very little so up to 40° C., whilst there is a very large increase between 40° and 60° Fahr. 3. No fixed proportion can be found between the quantities of sodium hydrate and sulphide formed. 4. The decrease of the sodium carbonate is evidently dependent as much on the formation of the sulphide as on that of the hydrate; that is, the sulphide is formed at the direct expense of the carbonate, not that of the caustic. 5. No more available soda can be extracted by 1000 or 2000 than by 500 c.c. (indeed, except in the six hours' trials, rather less); and the lower the temperature the better. The worst results are obtained when an excess of temperature, of time, and of water, are all acting together.

Kolb's special experiments upon the solubility of calcium sulphide also merit attention. He found the following results:—

1. CaS is very little indeed decomposed by pure water; the presence of NaCl slightly decreases, of Na_2SO_4 slightly increases its solubility. The decomposition, as far as it goes, takes place according to this equation:—

$$2CaS + 2H_2O = CaH_2S_2 + CaH_2O_2$$

And 1 litre water dissolves by forty-eight hours' digestion:—

At 10°, 18°, 40°, 60°, 90°,
·75, ·23, ·30, ·48, ·33 gram. CaS.

2. A saturated solution of sodium carbonate scarcely acts at all on calcium sulphide; but the action increases rapidly if the concentration of the solution is diminished, and the temperature and time of digestion are increased. The presence of a slight proportion of sodium hydrate retards the decomposition considerably. The equation is—

$$CaS + Na_2CO_3 = CaCO_3 + Na_2S.$$

3. A dilute solution of sodium hydrate (= 3·15 gram. Na_2O per litre) decomposes only traces of CaS, either in the cold or at a boiling heat. More concentrated solutions, containing from 16 to 79 grams. Na_2O per litre, if digested for forty-eight hours and heated to 40°, 60°, or 100° C., cause a gradual decomposition, which increases proportionately to the quantity of sodium compounds in the liquid.

The practical conclusions from Kolb's experiments are, that it is expedient to lixiviate the black ash—1st, as quickly as possible; 2nd, with as little water as possible, 3rd, at the lowest possible temperature. Unfortunately these conditions cannot be applied to operations on a large scale, and it will be shown afterwards what the practice on that scale has shown to be the best method.

The presence of sodium sulphide in the liquor is particularly injurious, because it acts upon the iron oxide always present, and causes the production of a ferro-sodium sulphide. This compound, even when present in extremely minute quantities, colours the liquors green, yellow, or brown, and may similarly discolour the soda ash subsequently obtained. More will be said on this further on.

We shall say very little about the lixiviating apparatus formerly in use, as the only one which is now employed in works conducted on modern principles is that to be described at length hereafter.

The oldest apparatus consisted of several (usually

three) tiers of iron tanks, one raised above the other in the manner of steps, provided each with a cock at a certain height over the bottom. The lye from the top tier was run on to the middle tier, from this on to the bottom tier, and was then ready for evaporation. On the other hand, the black-ash was first tipped into the bottom tanks; when these were run off the residue was shovelled up into the middle tanks, and at last into the top tanks, where fresh water was run on to it, and from whence the residue was taken out to be removed altogether. The only heating of the water or lye was by the black-ash itself.

This manipulation was not only very laborious, but it rendered, moreover, the mass very dense and compact, and thus seriously impaired its permeability for the lixiviating liquid. The solutions thus obtained rarely exceeded 1·15 specific gravity. A considerable improvement was effected by the apparatus of Clement-Desormes, which, indeed, held its ground on the Continent until quite a recent period. Instead of throwing the black-ash direct into the vats, where very soon a strong solution is formed at the bottom, and very little further action goes on, Clement placed it in perforated baskets of sheet iron, which, with their contents, were immersed in the water of the several vats, and kept suspended near the top by means of handles and cross-bars. The vats themselves (generally ten or twelve in one series) were placed each slightly higher than the former, and were connected by bent pipes in such a manner, that the bottom of each vat communicated with the top of the next lower one. Water was run into the top vat, and this, after acting upon the contents of the basket, flowed over from the bottom of the vat to the next lower one, and so forth, till it issued at the bottom as a concentrated solution of ball-soda. On the other hand, the black-ash travelled the reverse way; each basketful was put in fresh at the lowest vat. After a time the top one was taken out and emptied; it was replaced by that from the second, this by that from the third vat, &c.; the lowest one, which thus became empty, being provided with a fresh basket. A travelling crane facilitated the removal of the baskets. A steam-pipe running alongside the vats served to heat them, according to requirement. Each basket held from 56 to 112 lbs. of black-ash; each ton required therefore the use of from forty to fifty baskets.

This plan gave very strong solutions, and thoroughly exhausted the black-ash; but it had great drawbacks. The labour of continually lifting the baskets was very considerable, and the space and plant required for the operation in large works would be very large, as it goes on very slowly; but worse than that, the black-ash, which during the lifting of the baskets lost the hydrostatic support of the liquids, sunk down into a more and more compact mass, and thus to a great extent lost one of the most valuable properties of black-ash, viz., its porosity. Moreover, a great deal of fine stuff passed through the holes of the baskets, and, on the one hand, rapidly plugged them up, on the other hand, made the liquors muddy.

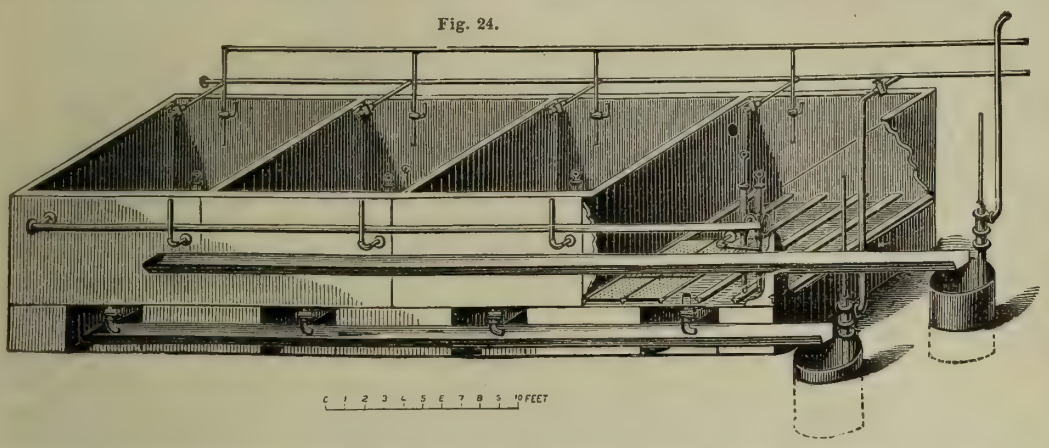
Shanks' Process.—Nobody who has once seen the ordinary lixiviating tanks now in universal use in this country, can wonder that they have entirely supplanted Clement's apparatus in all English works, and are doing so more and more on the Continent as well. The "tanks" or "vats" now used are vastly superior to any previous arrangement by their cheapness, efficiency, and almost grand simplicity. It seems that the inventor of this invaluable help to alkali-makers was the late James Shanks of St. Helens. Dr. Muspratt states it to be a foreign invention, introduced by Dunlop into the St. Rollox Works at Glasgow about 1843; but this is probably a mistake, as nobody has ever claimed for himself or any one else the honour of this invention, except Shanks, who has been rewarded for it by the greatest distinctions of International Exhibitions. Shanks' vats, by applying the principle of leaving the ball-soda at rest and causing the liquor to travel through it, obviates the labour of removing and the necessity of destroying the porosity of the black-ash. This is effected, not by the placing of the vats at different levels, but by producing a flow of the liquor through them entirely by utilizing the difference in specific gravity between water and weaker and stronger lyes.

The ordinary lixiviating tanks (sufficient for working the produce of four or even five ball furnaces), are shown in Fig. 24, in an isometrical drawing. They consist generally of a set of four, made by dividing a long tank (40 feet long and 10 feet wide by 6 feet high), into four compartments of 10 feet square each.

Of course these measurements are only given here as very common, not as general ones. The tanks are made of $\frac{3}{8}$-inch iron plates, strengthened by angle-iron at the top; T-shaped bars are rivetted at a distance of 6 inches from the bottom, as shown in the engraving, and these serve as supports for the perforated false bottom. The true bottom is made sometimes to slope towards the front, but more generally it is left level. The false bottom has very frequently to be taken up for cleaning out the holes and the space underneath, and it must therefore consist of a number of plates, say 2 feet square, loosely laid side by side on the T-shaped bars. The plates are sometimes made of cast iron, but wrought iron ($\frac{3}{8}$-inch), is much preferable, as the cast-iron plates break very easily. The holes are from one-fourth to one-half inch wide, and about 3 inches from centre to centre. Each tank has an outlet cock of 3 inches bore, which must be so constructed as to admit of easy cleaning out by a red-hot iron when it is stopped up by crystals. Each tank has also two "jugs," as shown in the diagram. One set of these serves as a means of communication between the vats; the other for running off the strong liquor. The "jugs" consist of metal pipes 3 inches bore in the lower, and 4 inches in the upper part, with a side branch, and with a conical valve seat about midway up. A plug with handle accessible from the top fits on the valve seat, and if put in, closes the communication; whilst, when it is off, the liquor below the bottom

of each vat can flow through the jug and its side branch into the next vat. The corresponding jug in the last vat (that to the right in the diagram), cannot of course communicate direct with the first one; but it does so by means of the horizontal pipe running back from the last to the first vat. The

Fig. 24.



plugs are sometimes turned in the lathe to fit the bored out seat; but as this fit is easily disturbed by any dirt getting between the faces, it is better to groove the sides of the plug, and lap them with tarred spun-yarn, which closes the valve more safely. The second set of jugs are all in the front of the tanks; they have somewhat lower branches than the other jugs, and are on the outside either connected with taps or, as in the diagram, with several pipes, which can be turned up or down. As a rule they are turned up, and only in that tank which is running strong liquor the pipe is turned down into the spout carrying the lye away into the strong liquor well. Another spout runs underneath the outlet cocks, and leads into the weak liquor well. Each well is provided with a pump. A cold water-pipe with a cock for each tank runs along their tops, and the delivery pipe of the weak liquor pump is connected with this water-pipe, unless a special range of pipes is laid on for the weak liquor. Another range of pipes is laid on for hot water, or instead of this (as in the diagram), a steam-pipe sending a branch (or preferably two branches) into each vat. The tanks sometimes rest upon the floor; it is, however, preferable to mount them on brick walls, so that any leakages may be more easily detected.

It will be seen that all the tanks are on the same level, and the principle on which they are worked is as follows:—The ball-soda is placed in the tanks, on the top of the false bottom; and once there it is not removed, as in the process just described, but it remains in the same tank till it is completely exhausted. Thus it remains porous up to the very last, and allows the liquid to circulate freely, and to penetrate into every part of the mass. This makes such a difference that four, or even three treatments, suffice for exhausting the black-ash, whilst ten or twelve treatments are required in Clement's apparatus. The black-ash being stationary, it follows as a matter of course that the necessary change of liquid is produced entirely by a removal of the lye from one tank to another. It is the very great merit of Shanks' tanks that the liquids are made to travel from one vat to the other, without raising the vats one over the other, but entirely by relying on the hydrostatic pressure of the liquids.

As the lye in its progress through the tanks is more and more saturated by dissolving soda salts, its specific gravity becomes greater; and in consequence of this the level of the liquid in the "strong tanks" is below that in the "weak" tanks. It has been considered by some that the "declivity" from the weak to the strong tanks thus produced is the real moving cause for the liquid; but this is entirely erroneous, as each tank will find its exact level according to the specific gravity of the lye contained in it, and the shorter columns in the strong tanks exercise precisely the same action as the longer columns in the weak tanks. When the supply of water to the weak tank is stopped, the strong tank at once ceases running, although its level is much below that of the weak tank. The real moving cause is the small head of water produced in the weak tank by the influx of the fresh water on the one side, and the running out of the strong liquor from the strong tank *below* the level of the lye. But the immense advantage of Shanks' system over that of Clement's is this—that the whole play of levels being reduced to about 18 inches, or say one-fourth of the depth of the tanks, they can be, and always are, arranged so that each tank may serve as a weak, an intermediary, or a strong tank, as will be seen directly.

The practical operation is carried out as follows:—The balls, which should be cold enough to be handled (forty-eight hours is a very good time for them to lie after being drawn out of the furnace), but which ought not to be kept longer than necessary over and above that, are broken into pieces of the size of a man's head, many small pieces, of course, being produced as well. These are filled into barrows or small waggons, and tipped into the

tank which has just been "cast," that is, emptied of its contents of exhausted balls. The tank is filled up to 12 inches below its top, and the pieces of balls roughly levelled with a hook. Before tipping any balls into the tanks, the perforated plates are taken up and the space below them is cleaned out, as any waste left there would greatly injure the liquors. The false bottom is replaced and a layer of about 4 inches of furnace cinders, from which the fine ashes have been separated by a half-inch screen, is spread upon it to serve as a filter and prevent the holes from being too quickly filled up with tank waste. The balls are then tipped in. When a set of vats has to be started anew, of course at least three of them have to be filled to begin with. Supposing this to be the case, warm water (90° to 100° Fahr. in summer, 100° to 115° Fahr. in winter) is run on to the top of the first tank, say that on the left-hand side of the drawing. The warm water in percolating through the balls dissolves a portion of their soluble contents, and arrives below the false bottom charged with them. The "jug" communicating with the second tank has been left open, and the ball solution will, therefore, rise from underneath the false bottom in the jug; and as soon as the level of the water in the tanks is high enough, the liquor will overflow into the second tank, running there over the balls from the top or "covering" them. In doing so and percolating through the porous mass it becomes naturally stronger, and indeed, when working with *fresh* tanks, will probably become strong enough to be run out from the jugs of No. II. tank for evaporation. In the ordinary course, however, it will again rise from underneath the false bottom in the jug and overflow into No. III. tank, and thence into No. IV. tank. In any case it will be strong enough now, and the overflow jug of this tank will, therefore, be plugged, whilst the running-off jug is made to act by lifting its plug, and the liquor runs out of No. IV. tank through the open spout (shown in the drawing) into the strong liquor well.

Meanwhile the first tank has received four different waters, or rather sufficient water to fill it four times over, but in a continuous flow. It will now be entirely exhausted, as shown by the fact that the liquor rising in its tank jug only shows about 1° Twaddle. The jug is now plugged; No. II. tank is made first tank, and fresh water is run upon it. No. I. tank is first emptied of water by opening the bottom cock; the water, which still contains a little soda, is run into the weak liquor well and pumped up to serve as first water on No. II. tank. The contents of No. I. tank, which are now greatly reduced in bulk, form what is called "tank refuse" or "waste;" they are at once shovelled out of it, mostly direct into waggons which carry it away to its destination. The cinders are cast out along with the waste, the plates are lifted, the tank is washed out, the plates are replaced and covered with cinders, and the tank is recharged with fresh balls.

The following is an analysis, by G. E. Davies, of weak liquor of 1° Twaddle:—

Sodium hydrate,	2·640
" carbonate,	1·060
" sulphide,	2·690
" hyposulphite,	0·554
" sulphate,	0·284
" chloride,	6·780
" silicate,	0·100
" aluminate,	0·108
Total solids per litre,	14·216

In the meantime only three tanks have been at work; but these will have been quite sufficient. It is usual to run the liquor away for evaporation till it comes down to 1·23 or even 1·21 specific gravity. The *average* specific gravity (after mixing up all runnings) of a good tank liquor should not vary much above 1·29, nor below 1·26. But when it has come down to 1·23 (or even 1·21, according to the judgment of the manufacturer), the running-off jug is stopped, and the overflow jug of No. IV. tank opened, which communicates through the long return pipe with No. I. tank. The intermediate liquor of No. IV. tank will now "cover" the balls in No. I., and when rising from below its false bottom, it will, of course, become fully strong enough at first up to 1·30; it is therefore at once run off from this tank for evaporation. All the while No. II. has been functionating as "weak" tank, and it continues to do so until it is exhausted; then the water is diverted into No. II.; the weak liquor of No. II. is run off, and the whole operation repeated as before in No. I. It will thus be seen that each tank in its turn becomes the first, an intermediate, and the last of the series, the return pipe causing the set to act as if it were mounted in a circle. It should be noticed, that the liquors always become stronger as they flow downwards; that therefore their increase in specific gravity does not cause any mixing up of the liquids, the weaker liquids always floating on the top of the stronger ones, but forcing the latter by their hydrostatic pressure to rise in the jug and overflow to either in order to be run off, or into the next tank. The side branches of the running-off jugs are a few inches lower than those of the overflow-jugs, which facilitates the locomotion of the liquor in the whole system. Both the strong and the weak tank are worked according to their own requirements, and independently of each other; the intermediate ones take their chance.

One very important matter is the proper regulation of the temperature. It has been mentioned that the water (say the surface) of the weak tank ought not to be warmer than about 100° Fahr., with a downward margin of 10° in summer and an upward one of 15° in winter. The liquor becomes hotter as it gets stronger, partly owing to the heat of the balls, partly to the chemical action of the water on the anhydrous oxides and salts of the black-ash. The temperature of the strong liquor ought in no case to exceed 150°, and if it rises above this the weak tank must at once be made colder. After what has been said before about Kolb's experiments, it is unnecessary to enter again into the

reasons why the temperature during the lixiviation must be kept as low as is consistent with a thorough exhaustion of the balls. But it is well known to practical men that a high temperature does much more harm in the weak tank than in the strong one; that is to say, it causes much more sodium sulphide and caustic to be formed where water acts upon nearly exhausted balls, than where a strong lye acts upon fresh balls. On the other hand, unless there is a good heat (140° to 150°) in the strong tank the balls never dissolve as well as they might, and are not so well exhausted. This aim can be attained with more certainty by substituting steam for warm water in the lixiviating tanks, and in the case of revolver-balls this is altogether indispensable. In this case, too, steam-pipes in each tank just dip below the liquids; thus they are not in the way in cleaning out, and no currents are caused by the action of the steam. The water is run to the weak tank almost or quite cold; it is only slightly heated (to about 110° Fahr.) in the intermediate tanks; but in the strong tanks it is kept at 150°, or even more, without doing any harm.

Another important precaution to observe is this, that the balls, when once they have become wetted, must always be kept submerged below the surface of the liquid, and if they stand out, must be carefully pulled under with a hook. Unless this is done the moist calcium sulphide is speedily oxidised to a great extent, and the resulting sulphate, sulphide, &c., destroy an equivalent quantity of sodium carbonate by double decomposition.

Tank Waste.—This in most factories is a real *waste* product, and is besides a source of nuisance and expense. It ought to be of fine grain, from the size of a mustard seed up to that of a pea; any larger lumps or clots are almost sure to contain too large a proportion of undissolved sodium salts. From the appearance of the waste it is pretty safe to judge upon its being properly lixiviated; but it is always advisable to test a sample from each vat. This can be done thus:—50 grams. of the well-mixed sample are shaken up for some time with tepid water, and diluted to 1000 c.c. Of the clear solution, 100 c.c. (= 5 grams. waste) are evaporated to dryness, with addition of a little ammonium carbonate. This is done in order to decompose any calcium bisulphide or hyposulphite, which would interfere with the alkalimetrical test. The dry residue is heated to expel the ammoniacal salts, dissolved in water, and the filtered solution tested for soda with standard sulphuric acid. The proportion of soluble soda thus found ought not to exceed one-tenth of a per cent. It is also interesting now and then to test for the total soda, including the insoluble portion, which is of course irrecoverable from the waste, but whose proportion, if found excessive, affords some guidance for the carrying on of the balling process. The total soda can be ascertained thus:—18·00 grams. of the waste are heated in a porcelain or even iron dish with sulphuric acid, of 100° Tw., till it is thoroughly decomposed and converted into a paste. The excess of sulphuric acid is driven off by ignition, boiling water is added, and the contents of the dish scraped out with a wooden spatula, and transferred to a glass cylinder of 250 c.c. capacity. Here a little lime cream is added, which neutralizes any free acid remaining, and precipitates all magnesia. The cylinder is filled up to the mark, and allowed to stand till the liquid settles; 50 c.c. of the clear liquid are taken out, 10 c.c. of a concentrated solution of barium hydrate are added, filtered through a dry filter; 50 c.c. of the filtrate taken away, and a current of carbonic acid passed through. The liquid is then boiled, filtered, and the clear filtrate tested with standard acid. Each c.c. standard acid will correspond to 1 per cent. of soda in the waste, from all sodium compounds, soluble and insoluble. If no allowance for the bulk of the waste itself were made, 18·60 grams. would have to be employed; 18·00 provides for the above.

In most factories it is usual to remove the tank waste as soon as possible, as after a short time—sometimes after one day's keeping, sometimes a little later—a decomposition sets in by the aid of the moisture present in large quantities, and of the atmospheric oxygen, which causes the formation of soluble calcium hydrosulphide, bisulphide, and hyposulphite—not to mention insoluble and innocuous products of the action. The carbonic acid of the air acting upon these compounds, more especially the two former, causes the evolution of hydrogen sulphide, which of course amounts to a great nuisance. A sign of the oxidation is this—that the mass gets heated; after a few days of exposure in the loose state, it may even become red-hot. The more it heats, the more it also generally smells. This heating and its consequences—viz., the formation of soluble calcium sulphides—can be avoided to a very great extent if the tank waste is not allowed to lie in loose heaps, or mixed with other refuse (ashes, &c.), which keeps it in a porous state and accessible to air. If it is laid down in an unmixed form, and beaten down with shovels so as to form a level, dense surface, this is soon made almost impervious to air by the formation of calcium sulphite and sulphate; and when treated in this manner the tank waste is in itself not in the least offensive—no sulphuretted hydrogen is given off from it, and in most chemical works many of the floors of the working sheds are formed in this way. The tank-waste floors do not, however, stand any other but foot traffic, as they are cut up very easily by cart or even by barrow wheels; they can only be used for barrow traffic by bedding in iron or wooden runners for the barrow-wheels. The same kind of floor answers very well for the drying plates in brick-works. These applications dispose, of course, of only a very small quantity of the tank waste; and the further proposal which has been made—viz., to fill up the space between the flooring joists of dwelling houses with it, in order to protect them from dry rot—does not seem to have had any practical success. Formerly the bulk of the tank waste was disposed of by putting it in heaps

on waste ground in the neighbourhood of the works; and by carefully keeping out any ashes or other refuse, and working the heaps into the shape of embankments, with smooth and steep walls, any immediate nuisance can be prevented, as stated above. One thing will, however, always remain—viz., the drainage. Slowly but surely the sulphide becomes soluble, and oozes out at the bottom of the heaps as a yellow or brown, sometimes almost black, liquor, which smells most offensively, and even more so when it gets into the ordinary drains, where there is always abundance of carbonic acid. This nuisance may continue for a whole generation.

The usual plan on the Tyne is to send the tank waste to sea. It is, however, best to treat it for the recovery of sulphur, if there is no sufficient outlet for the muriatic acid.

The dark grey or black colour of fresh tank waste is changed into light yellow or nearly white after it has been weathered, in consequence of the iron sulphide being oxidised into iron oxide and free sulphur. At the same time the sodium sulphide combined with the iron sulphide is oxidised as well as the calcium sulphide; the result being principally hyposulphites. These are partly acted upon by the carbonic acid of the air; carbonates are formed, and at the same time bisulphides and sulphides; later on calcium sulphate or gypsum. The latter acts as a kind of cement, and causes old tank walls to be very hard. This property some have tried to utilize, and the application of tank waste after calcining it with clay and washing it as Portland cement, has been proposed by Aspdin. It does not appear that this application has been a success; but in the previous stage the tank waste forms the most important raw material for the manufacture of sodium hyposulphite, which is principally made on the Tyne by lixiviating old tank heaps and decomposing the calcium hyposulphite by means of sodium sulphate.

The following table shows the composition of tank waste as found by several chemists. It must, however, be observed that absolutely fresh tank waste gives a totally different result from such as has been kept even a short time exposed to air:—

	Hofmann.	Unger.	Muspratt.		Petersen.	Brown.	Kopp.
			A. Six weeks old.	B. Fresh.			
Calcium bisulphide,	—	4·67	5·97	0·62	—	3·58	—
" sulphide,	35·00	29·30	25·79	36·70	8·44	24·70	31·60
" hydrate,	13 75	14·85	6·59	9·11	—	8·65	12·35
" carbonate,	21·54	19 56	41·20	23·42	36·88	24·22	16·10
" sulphate,	—	—	2·53	4·59	3·73	4·28	—
" sulphite,	—	3·69	—	—	19·63	—	—
" hyposulphite,	—	4·12	—	—	1·53	trace.	—
Sodium sulphide,	4·55	1·78	1·44	2·87	—	—	7·40
" carbonate,	—	0·57	1·31	—	—	—	—
Iron oxide,	—	3·70	8·91	7·40	1·34	5·72	—
" sulphide,	4·22	—			—	—	—
Alumina,	—	—					
Phosphates of earths,	—	—					
Magnesium silicate,	—	6·91	3·63	1·78	—	5·99	—
Carbon,	2·84	2·60	—	—	5·87	12·71	13·45
Sand,	—	3·15	3·09	—	6·29	5·74	
Water,	3·82	6·05	3·86	13·51	10·26	3·46	19·10

Tank Liquor.—This is the solution of black-ash running from the "strong" tanks, and collected in the strong liquor well. It is always coloured more or less yellow or brown, sometimes green; but the latter colour shows that it has been overheated. A light straw colour is the best. It shows from 1·26 to 1·29 specific gravity, and contains about a quarter of its weight of solid constituents. The following are analyses of it:—

	Brown. (Total Solids.)		Mohr. (Total Solids.)	Davies. (Per Litre Liquor.)	
	A.	B.		A.	B.
	Per Cent.	Per Cent.	Per Cent.	Grams.	Grams.
Sodium carbonate,	68·91	65·51	71·25	209·500	204·326
" hydrate,	14·43	16·07	24·50	44·800	52·740
" sulphide,	1·31	1·54	0·23	4·485	3·822
" sulphite,	2·23	2·13	0·10	1·323	0·979
" hyposulphite,	trace.	trace.	0·37	1·580	1·774
" sulphate,	7·02	7·81	—	12·707	14·258
" chloride,	3·97	3·86	1·85	19·597	23·412
" cyanide,	—	—	0·09	—	—
" ferrocyanide,	—	—	—	0·133	0·416
" sulphocyanide,	—	—	—	0·211	0·196
" silicate,	1·03	·80	—	5·961	3·774
" aluminate,	1·02	1·23	—	3·371	4·218
Alumina,	—	—	1·51	—	—
Silica,	—	—	·17	—	—
Iron sulphide,	—	—	trace.	0·074	0·042
Insoluble in acids,	·81	·97	—	—	—
	100·73	99·92	100·07	303·742	309·957

The tank liquor, as it runs off from the strong tank, never goes direct to the evaporating pans, but always first to *settlers*. These are tanks in which it is allowed to stand for twelve hours or more, during which time not only any mechanically carried away portions of tank waste subside to the bottom, but a considerable quantity of a sodio-aluminium silicate crystallizes out; a further quantity of this separates as hard crusts upon the concentrating pans. The following are analyses by G. E. Davies of (A) the deposit from settlers; (B) the crust from the concentrating pans:—

	A.	B.
Silica,	23·60	39·572
Alumina,	18·44	33·584
Sodium oxide,	13·12	20·776
Water,	—	5·844
Iron sulphide	5·84	—
Calcium sulphide,	38·00	—
Total,	99·00	99·776

Sometimes large store tanks for holding the liquor are built underground; but as these cannot very easily be controlled as to their leakages, it is much better to make the strong liquor well only just large enough for a pump to work in (in this case it is generally made of cast iron), and pump the liquor, as it is made, into settling tanks placed at a higher level, where they are visible and accessible from below. In this case it is possible to give the liquor a preliminary heating in the settling tank by means of the waste heat of some furnace (for instance, the carbonating furnaces); if applied over the top, the settling itself will not be interfered with in the least. In any case the settlers must be placed high enough to feed the boiling down pans; but where the liquor is first oxidised or carbonated in towers, they must be placed correspondingly higher.

This oxidising or carbonating process is resorted to for several purposes, and sometimes one, sometimes the other, sometimes both are used. The process, as first proposed by Gossage in 1853, and carried out in several Lancashire works, consists in exposing the tank liquor, whilst it trickles down in an iron tower packed with cake, to the action of a current of air. The liquor, when arriving at the bottom, is tested with a solution of lead, and if it should still show a reaction upon sulphides, it is pumped up again and subjected to the same process. The sodium sulphide is thus oxidised, and the iron sulphide combined with it is precipitated as oxide which can be settled out again. In some works, instead of a current of air, the gas from a lime kiln (impure carbonic acid) is employed for this purpose, and evidently with much greater effect, at the same time converting the caustic soda into carbonate, and decomposing the sodium aluminates with precipitation of Al_2O_3 (which sometimes causes trouble by stopping up the interstices between the pieces of coke). The best plan of all seems to be that of employing the gas from some furnace containing both carbonic acid and free oxygen, and in this case the evaporation of the lye will be begun very effectively in the oxidising tower itself.

Instead of Gossage's tower, Hargreaves has introduced (1866) a lower cylinder, fitted with a perforated false bottom, below which he injects a current of air by means of a steam blast; the double bottom divides the current into many bubbles. This process is very much in use in factories where caustic soda is made, and where it is not intended to carbonate but only to oxidise the liquor. It consumes a great deal of steam, more than the pumping in Gossage's plan, but it does not lead to the same loss of soda remaining with the coke, &c., as the latter. The most complete means for this purpose would seem to be Koerting's blower, which works more economically than a pump, and which can be used with either air or carbonic acid from any source. It would slightly dilute the liquid, whilst running it down in a coke tower concentrates it; but that would be of less consequence than the apparently inevitable loss (as found in practice) of 1 or even 2 per cent. of soda in the latter case. The majority of works, although irrationally, use none of these processes; but either carbonate the ash later on by means of sawdust, or else separate the product into "fished" ash, which requires no carbonating, and "caustic ash," or caustic soda, as will be seen hereafter.

One of the constituents of tank liquor which occurs in such small quantities that it is generally omitted in its analysis, nevertheless plays an important part further on, when the colour of the soda ash comes to be considered. This is sodium ferrocyanide. It is extremely difficult, if at all possible, to destroy this compound. Although it can be done, according to J. C. Stevenson, by heating the liquor under pressure to 150° C., there are practical difficulties in the way of carrying this out on a large scale, apart from the expense, and it is nowhere done. In consequence of this all the iron can never be removed from the tank liquors, even by completely carbonating it and destroying the ferro-sodium sulphide, and the destruction of the sodium ferrocyanide during the ultimate ignition of the ash (in the finishing or carbonating furnace) causes the ash to be coloured yellow by ferric oxide. This can only be avoided by using a mixing coal quite free from nitrogen. A portion of the cyanogen compounds formed in the ball-furnace is often decomposed during the cooling of the balls by the action of the air, as evinced by the ammoniacal smell they sometimes show.

Salting-down.—The evaporation itself is carried on by two systems, viz.—either by surface evaporation or by bottom heat. The first system is that universally followed on the Tyne, and in use in many places elsewhere; the second system is more usual in Lancashire and on the Continent. The pans generally used for surface evaporation are shown, both in connection with the ordinary and with the revolving ball-furnaces, upon the respective Plates, as they are always heated by the flame escaping from the ball-furnaces. They have been described in detail in connection with the ball-furnace, from which they are inseparable, and it only remains to

say something about the work performed in them. Each pan is supposed to do all the work necessary for the produce of its own furnace, that is, to evaporate the liquor resulting from the lixiviation of as many balls as the furnace produces. The liquor is run in from the settler, and kept up by feeding the pan from time to time so that its level is pretty well kept up. The supply is so regulated that after each twenty-four hours the pan is ready to be drawn, that is to say, the salt has accumulated in it to such an extent that it reaches to the top of the liquid, and the whole forms, in fact, a pasty mass. It is necessary during the evaporation to work from time to time with a light rake in the pan, beating down any crusts formed on the top (which would, of course, hinder the evaporation), and working the salt from the neighbourhood of the furnace, where, of course, it forms in greatest abundance, towards the back-end of the pan. When it is ready for drawing, one of the doors (which have been luted with clay) is slackened, so that the bulk of the liquid runs out into the drainer mounted in front of the pan, and into which its discharging doors project; then the doors are taken off altogether, and the whole of the contents of the pan are raked out as quickly as possible. The drainer is supplied with a perforated false bottom similar to that of the lixiviating tanks, and the real bottom of the drainer is either sloped off at one end, or it contains at least a depression (or well) for the drainer pump to stand in. This is done so that the mother liquor ("red liquor") may drain off as completely as possible and may be pumped away. In many works it is always pumped back straight into the pans and boiled down along with the next charge; in some cases it is, however, pumped away into separate cisterns and boiled down by itself. This is especially often the case with revolver pans, which (as well as the drainers) are provided with a partition for this purpose. The front part of the pan never receives any red liquor, and therefore yields a soda ash testing up to 56 per cent. available soda; the back part of the pan receives *all* the red liquor produced in the drainer, and only yields 50 to 52 per cent. ash. Where, as is usual on the Tyne, the red liquors are simply pumped back into the same pans from which they came, the strength of the soda ash obtained in well-conducted works is not under 52 per cent.; but frequently up to 53 per cent., and with revolvers 54 per cent., or even more. This system is very cheap, simple, and effective, and causes very little wear and tear of the pans; but it is not at all adapted for works where the red liquors are required for caustic soda, and it does not on the whole yield as pure an ash as the "fishing" process, or rather it does not allow of such an easy and complete separation of the products. It is certainly a mistake to say (as it is sometimes done) that in this kind of evaporation no fuel at all is required, for every practical man knows that he must burn more coal to do his boiling down than when he has only balls to make, and, moreover, it must be a good bituminous coal, giving a long and hot flame. There is much less labour required than with bottom evaporation, and the salt does not easily burn fast to the sides and bottom of the pan. Where the liquor has not been oxidised beforehand, it is usual to put sawdust into the pan during the evaporation. This not only acts further on in the carbonating or finishing furnace by means of its carbon, but it is also of very great importance for the draining process. The salt from these pans, being of much finer grain than the "fished" salts from boat pans, would part very badly with its mother liquor, were it not that the sawdust makes it porous and more permeable. In some cases, when it is used without mother liquor, it is even washed with water to remove the latter more completely, and drained by means of a centrifugal machine (first introduced by Gamble). This, however, is only rarely done. In most works on the Tyne the salt is wheeled from the pan-drainers to the "stock-drainers," where it rests one or two days, and is more completely freed from red liquor. It distinctly improves by that operation.

The salt thus collected on the drainers ("black salt") is essentially constituted according to the formula $Na_2CO_3 + H_2O$. When of very good quality it is nearly white and of coarse grain; but when impure (from ferro-sodium sulphide) it is more or less coloured yellow or brown, even red, and generally some of the red crystals of one of the several sulphides can be observed separately.

The action in the black-salt pan has been studied by Moorhouse, who gives the following tables of his results:—

I.—PROPORTION OF CAUSTIC SODA TO TOTAL AVAILABLE SODA PRESENT IN THE LIQUOR, IN THE BLACK SALT AND IN THE ASH MADE FROM IT.

Tank liquor,	19·6	22·2	19 0	12·9	20·4	20·2
Black salt,	13·3	13·7	14·3	11·6	17·6	11·8
Soda ash,	—	6·0	3·2	3·5	3·0	4·4
Salt from front of pan,	12.1	11·7	15·7	13·6	6·8	—
Salt from back of pan,	8·6	12·2	17·1	8·0	6·1	—

II.—TOTAL SULPHUR (IN ALL COMBINATIONS) CONTAINED IN—

Tank liquor,	1·59	2·24	2·14	2·08	2·13	2·05
Black salt,	1·77	—	1·79	2·20	2·14	2·09
Soda ash,	2·16	2·33	2·25	2·38	2·34	—
Salt from front of pan,	—	—	1·80	2·50	1·90	2·42
Salt from back of pan,	—	—	1·71	1·95	2·19	2·19

From No. I. it will be seen that, through the action of the furnace gas, a large proportion of the sodium hydrate is converted into carbonate in the pan; the average diminution of Na_2O existing as NaHO, being 4·7 per cent. on the total available (that is, that which is shown by test acid) soda present. In carbonating a further average decrease of 9·8 is produced; but it is unfortunate that even the best of the six samples tested by Moorhouse was quite inferior with regard to this to the ordinary soda ash found in trade, and that, therefore, his experiments do not possess quite the same value as if his furnace processes had been in good order at that time.

The salt from the back end of the pan, which is

that which was first made and has been paddled there, might be expected to be less caustic than that from the front end, which is made later on, and it is so mostly, although not regularly.

The second table shows that all the sulphur is carried through the process into the ash, and none of it volatilized, as has been stated by Muspratt. On the contrary, its proportion is found to increase, undoubtedly partly from mechanically carried over sodium sulphate, and partly from the action of the sulphurous acid contained in the furnace gas.

A second system of surface evaporation is not practised very much in this country, but more so in France. It is, at the same time, the oldest system of all, and consists in combining evaporation and calcination in the same furnace. The bed of the furnace is shaped like a disk, and walled with very tight joints; it is brought to a bright red heat before running in any liquor, so that a crust is formed at once which prevents the liquor from soaking too much into the brickwork; the evaporation is then continued with further quantities of liquor, and when a sufficient quantity of salt is collected, it is at once furnaced off and made into finished ash. This process gives a good quality of ash, but it is not adapted for the large-scale production of our times.

The process of bottom evaporation is also carried out in two different ways, viz., in flat pans and in boat pans. The former, which are the common ones in Germany and France, are built to some extent like salt pans, with hoods to carry away the steam, and provided with a depression along the side opposite to the fire. A common dimension is 25 feet long by 8 feet wide, by 20 inches deep. The bottom must be perfectly level and the rivets must be counter-sunk, as it is necessary to rake the salt continually away from it into the depression just mentioned; otherwise it would burn fast to the bottom, and the latter would be burnt away in an extremely short time, apart from the waste of heat acting through the iron and salt together. These pans have generally separate fires, and the smoke is burnt as much as possible; frequently the flame escaping from them serves for a preliminary heating of other pans. Each pan is filled up twice every twenty-four hours, and the salt accumulating in the depression is taken out, with a long, bent, perforated shovel, four times during that time, in order to be drained in a kind of hopper, from which the mothers run back into the pan. The latter thus accumulate more and more, and after eight or ten days (only with very good liquors after twenty-one to twenty-four days) the operation must be interrupted, because the fished soda ash becomes too weak. The remaining liquid is then evaporated till it shows (hot) 1·41 to 1·44 spec. grav.; the salt then separated on cooling mostly consists of sodium sulphate, and is worked up again in the ball-furnaces. This plan seems to involve much labour, expenditure for fuel, and wear and tear of the pans, and is not at all favoured by British alkali-makers.

The only system of bottom evaporation in extensive use in this country is that in the "boat pans," first introduced by Gamble. These are sometimes made of cast iron, 12 feet long, 8 feet wide, and 3 feet deep; sometimes of wrought iron, from 20 to 30 feet long, from 7 to 10 feet wide, and from 2½ to 3 feet deep in the centre. Their shape (shown in the wood-cuts given previously) resembles to some extent that of a boat, and they are set in such a manner that the centre or deepest part of the bottom is not at all touched by the flames, as it either rests on an arch or on a solid pillar, as explained above in describing the ball-furnace. The fire only touches the slanting part of the sides, not quite up to the point where they curve upwards, so that there remains enough room for the brickwork to support the pan, and at the same time enough room inside for a margin during the boiling down, as the surface of the liquor should of course never be lower than the highest part of the fire flues. In these pans the salt separating during the evaporation naturally and without any labour collects in the central depression, which is not touched by the fire, and is thus protected both against burning of the plates and against a disturbance of the settling by the ebullition of the liquid—the centre being just the quietest part of the pan. It is also very easy to "fish" out the salt from this central depression; and this kind of pans is indeed quite specially adapted for the Lancashire process, in which it is purposely avoided to carbonate the liquor even partially by means of the furnace gases, as it is the intention to separate the products into fished ash (of 55 to 57 per cent.), on the one hand, and "caustic ash" or caustic soda, on the other hand. "Caustic" ash is the product obtained by boiling down the mother liquor from the fished ash to dryness; the preparation of caustic soda will be described separately. The "caustic ash" sustains from 5 to 8 per cent. of sodium hydrate; and although its colour is very inferior, it is in good demand by paper-makers, soap-makers, and others, to whom its causticity is quite welcome. Its alkalimetrical test is 46 to 50 per cent.

Another kind of evaporating pan was proposed by Gossage in 1853. It is a double pan, consisting of two compartments connected by a large tube, one of which only is heated, whilst the other one serves for receiving the salts. The liquors are pumped continually from the cold pan into the hot one, and consequently overflow from the latter back into the former, where the salt crystallizes out, and the mothers are pumped back again. This system seems to be arranged in a most rational manner; but there must have been practical difficulties in the way, as it has not made its way among alkali-makers.

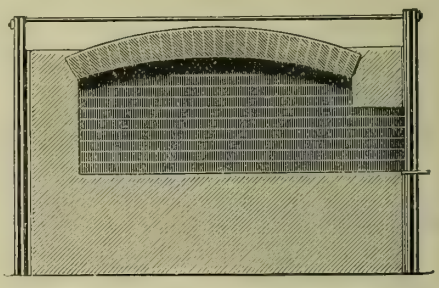
A modification, which refers less to the construction than to the working of the pans, has been introduced by Kuhlmann. It consists in fishing out the salts during evaporation of a fixed quantity of liquor, until the volume of the latter has been reduced to a certain point. By varying the relative volumes, salts of different degrees of strength can be obtained by fishing. Thus, when ordinary tank liquor of 1·286 specific gravity is boiled down to

seven-twelfths of its volume, and the salt precipitating in the meantime is fished out, a product testing 57 per cent. real soda is obtained. If the remaining liquor be boiled down to three-sevenths of its volume (= one-quarter of the original one), the product fished during this time will yield 50 per cent. ash. The residual liquor, dried in the furnace, yields a highly caustic ash. Kuhlmann for this purpose marks the sides of his pan correspondingly. Kolb has made special experiments on this subject, which do not quite harmonize with Kuhlmann's statements. According to Kolb, when a liquor containing sodium sulphate, carbonate, chloride, and caustic, is boiled down, the sulphate is generally separated first—all the more quickly the more caustic the liquor is. At the same time the precipitation of carbonate commences; this, however, is influenced by the presence of sodium chloride. If none of the latter salt is present, the first precipitates are poorer than the subsequent ones, because they contain more sulphate. If, however, much sodium chloride be present, the behaviour is an opposite one. The first precipitates are richest in soda, and later on more and more chloride is mixed with them. If the liquor contains, at the same time, a great deal of sulphate and chloride, the percentage of the precipitates in carbonate first increases, then it becomes stationary, and at last it decreases again. The caustic soda, which favours the precipitation of all three salts, remains in the mother liquor up to the last.

Carbonating or Finishing.—This operation completes the manufacture of ordinary soda ash. It would seem to those not acquainted with practical alkali making, as if both the furnace and the mode of operation in converting the drained "black-ash" must be of the simplest character. This is, however, only the case with very pure "fished" salts. These have merely to be dried by moderate heat to expel the water of crystallization, and the principal matter to be observed is this, that the heat must be kept sufficiently low not to melt the sodium carbonate; but this is easily avoided, as sulphide and caustic are practically absent. The matter is very different when the "black salt" from open pans (that is, those with surface evaporation) has to be treated, since it contains a considerable proportion of sodium hydrate and sulphide, and at the same time the sawdust, which is intended to supply the carbon for carbonating them; and a great deal of care has to be bestowed upon carrying out these operations successfully, so as to obtain ultimately a good ash.

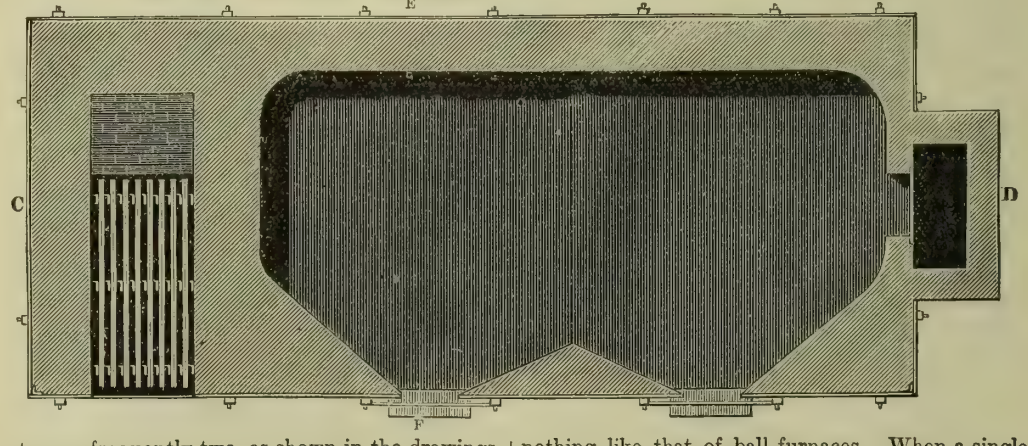
A carbonating furnace of very good construction is shown in Figs. 25 to 28. Fig. 25 is a section through E—F, Fig. 26; Fig. 26 is a horizontal section through A—B, Fig. 27; Fig. 27 is a section through

Fig. 25.



C—D, Fig. 26; Fig. 28, front elevation. It will be seen that the fire-bridge in this furnace is unusually high, and indeed only leaves a crescent-shaped slit for the fire to go through. Sometimes only one bed is used,

Fig. 26.



but more frequently two, as shown in the drawings. The black salt, where the levels allow it, is not charged through the door, but through a hopper, not indicated in the drawings, over the centre of the back bed. It is not necessary to bind these furnaces quite so strongly, or to provide them with hollow bridges and bridge plates, as the heat in them is nothing like that of ball-furnaces. When a single bed is used, it should be about 12 feet long by 8 feet wide; when two beds are used, they are about 8 feet square each. In a few cases the furnace bed is made of thick cast-iron plates; in the majority of works, however, it is made of fire-bricks on edge, closely wedged together. The waste heat from this furnace

can be either used for drying chalk, or for a preliminary heating of tank liquor, or, of course, for any other purpose.

Fig. 27.

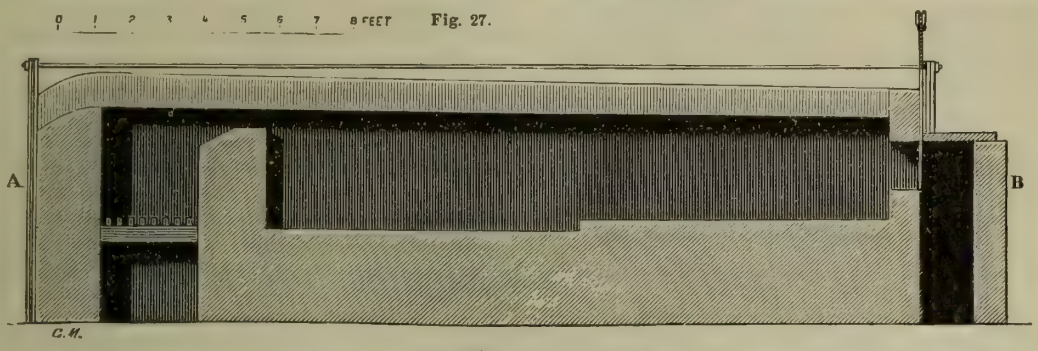
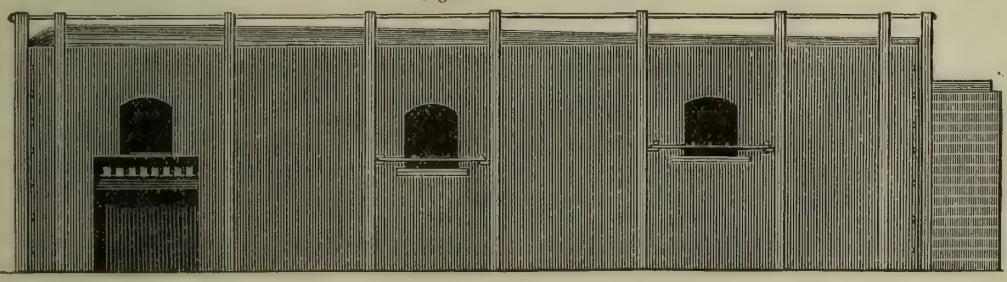


Fig. 28.



The carbonating operation is carried on as follows:—The black salt is first charged upon the back bed, where it is not disturbed, and where the moisture is expelled to a great extent. The work only begins properly after it has been shifted to the working bed. Each charge weighs about 16 cwts. after furnacing. The second bed is charged when the first charge is about half worked, and the damper is then raised, because at that moment more fire is needed, and the salt on the back bed impedes the draught; but when the latter, after drawing the charge from the front bed, has been shifted to it, the damper is let down again, and the first stage of the work, "the drying," begins. The heat at this stage does not very much exceed the melting point of lead; the fire is kept "green," that is, light and smoky, and the stuff is turned over now and then. The moisture is seen to escape in copious fumes; if there were too much heat in this stage the salts would be locally dried and fluxed, and would be found to be full of sulphide and caustic. This stage takes about two hours. When all steam is off and the stuff appears loose and pure a little more heat is applied, and the stuff is turned over very assiduously, as this is the proper "carbonating" stage; that is, now the sulphide is partly oxidised to sulphate, partly converted into carbonate, the sawdust is burnt, and the resulting carbonic acid, along with that of the fire, converts the caustic soda into carbonate. At this stage the furnace must be filled as much as possible with carbonic acid, and a good result can only be attained by great care and industry on the part of the furnace-man. Gradually the fire is increased, and the last stage is that of "firing" the mass, when it has to be brought to a good red heat, constantly turning it over and completely burning out the sawdust. This succeeds better with sawdust from pine wood than with that from hardwood. The furnace-man shifts the stuff portion by portion to the fire-bridge, and allows it to get just hot enough to burn out the sawdust, but removes it promptly before it can even begin to flux, and shifts another portion into the same place; he opens his working door more or less, or lets it down altogether for a while, just as the state of his furnace requires it. The less caustic there is in the stuff the more it will "stand the fire;" if it is too caustic it is "soft" and liable to fluxing, and cannot be heated as it ought, viz., ultimately with a clear fire, coming out red hot right through. The whole operation should not be done in less than five hours, to do it properly. It can hardly be described in words as it has to be done in practice, very careful manipulation being necessary throughout. The same black salt will, in the hands of a good workman, yield an ash of 52 per cent. soda and only 1 per cent. caustic, which in the hands of another only yields 51 or even 50 per cent., and 2 to 2½ per cent. caustic. In any well-carbonated ash there ought to be no more than 1 per cent. sulphite, and no sulphide whatever, or only the merest trace.

The action in the carbonating furnace has been studied by MOORHOUSE, who unfortunately did so when he had some abnormally sulphuretted salt to deal with, yielding abnormally caustic ash; nevertheless, his results are very interesting. The furnace was charged at 5·30 p.m., and samples were taken from it at seven, eight, and nine o'clock, and ultimately of the ash drawn out at 10·15 p.m. The results of the testings are embodied in the following table:—

	Black Salt Used.	Seven o clock.	Eight o clock.	Nine o clock.	Soda Ash.
Carbon,.....	1·11	0·32	0·38	0·10	nil.
Insoluble matter,.....	0·95	0·93	1·00	0·97	0·97
Sodium carbonate,.....	78·30	79·04	80·05	81·07	81·86
" hydrate, ...	7·59	6·30	5·42	4·40	3·97
" sulphate,.....	7·71	9·02	10·27	10·85	11·06
" sulphite,.....	0·82	1·77	0·83	0·38	0·21
" hyposulphite, ..	1·05	trace.	nil.	nil.	nil.
" sulphide, ...	0·33	trace.	trace.	trace.	trace.
Per cent. undissolved sulphur on total sulphur,.....	31	17	8·3	3·6	2·0
Per cent. Na_2O in state of NaHO on total available Na_2O,....	11·4	9·5	8·2	6·9	6·0

It will be seen that the proportion both of unoxidised S and of Na_2O existing as NaHO is reduced in a regular progression in the hourly stages, but the former much more rapidly than the latter. The sulphide and hyposulphite are oxidised with comparative ease, but the sulphite remains, although in diminished quantity, up to the last; and this is indeed the case not only with Moorhouse's very bad salt, but with the very best carbonated salts made in the usual way, without separating red liquors, &c.

A mechanical carbonating furnace, built in the form of a staircase, has been devised for Stevenson by James Napier; but although it dried and carbonated the salt, it could not be brought to the heat necessary for finishing it, and it had to be given up again. Probably Jones' machine (described in the article Sulphate of Soda) would do for carbonating also; but as it has only just been brought out, no experience exists on this point. Another mechanical furnace, however, patented lately by Mactear, of St. Rollox, seems to have really overcome all practical difficulties in the way of carbonating soda ash without manual labour. Its principle is that of a revolving circular hearth, with scrapers or ploughs, similar to some extent to the mechanical furnace for the calcining of cupreous pyrites cinders, devised by Gibb and Gelstharpe.

When the soda ash has been obtained, either after carbonating the tank liquor by gas in Gossage's towers, or by "fishing" the salt and leaving the mothers to be dealt with in some other way, it is generally both very strong and also very white. That, however, which has been obtained by surface evaporation, without separating the red liquors, is never quite white, but always yellowish, and sometimes reddish or brown; it is therefore often known as "yellow carbonate." A yellowish ash is, indeed, often found better carbonated than one of much whiter colour, and naturally so; for in the latter the iron salts have not been properly decomposed, and their very slight colour does not influence that of the bulk, whilst in the better fired sample all iron salts are converted into ferric oxide, whose red colour spoils the whiteness of the ash. A well-carbonated soda ash ought to be of yellowish, or even better, of slightly bluish colour (either from a trace of ultramarine, or from one of sodium manganate), but not grey, which speaks of bad carbonating, as well as any remains of charred sawdust, which ought to be altogether absent. After grinding, it ought not to show too many black or otherwise coloured specks (owing to charcoal, brick-dust, &c.). The residue insoluble in water ought not to exceed 1·5 per cent.; sulphide ought to be entirely absent; sulphite, not exceeding ·15 per cent; caustic, 2 per cent. (in ash made for dissolving for the manufacture of soda crystals, it is often brought down to 1 per cent.); chloride, 2 per cent. to 3 per cent.; the sulphate will vary from 5 to 10 per cent., according to the strength of the ash. All this refers to ordinary soda ash (yellow carbonate)—say up to 52 or 53 per cent. of available soda. The fished ash, made up to 56 per cent. or more, contains of course much smaller quantities of any of the above impurities. It would seem useless to repeat any of the published analyses of soda ash, as the proportions of the impurities vary very much, and the above maximum values for good merchantable ash are more valuable than any chance analysis published by some author.

The soda ash is rarely brought into the market as it comes from the furnaces, but is nearly always ground to powder; this is really much more economical, as the grinding does not cost very much more than the packing by hands, and there is a very considerable saving of casks. An ordinary alkali "tierce," made from 40-inch staves, holds only 8 to 9 cwts. of unground ash, but 12 to 14 cwts. ground ash, according to the way in which it is packed. The packing is often assisted by mechanical contrivances for shaking the casks and pressing the ash in during the grinding; in nearly every case the mills are made to deliver directly into the casks. This applies to grinding in horizontal mills, similar to flour mills, which are now generally preferred to the formerly used edge-runners, because they work much more cheaply owing to the large amount of work they do, and allow sifting apparatus to be dispensed with. The stones of these mills are not the French "burrs" used in corn grinding, but blue lava stones, mostly from the Lower Rhine, which resist the action of the hot ash without injury. A pair of edge-runners is, however, very useful for crushing the hard fluxings from the furnaces, which cause great wear and tear of the millstones. In Lancashire the ash is often packed in hard-wood sugar hogsheads, which hold up to 22 cwts. As customers frequently require ash of lower strength than that produced in the works, the strength is reduced accordingly by means of common salt (previously dried in a furnace), immediately before grinding. Where kelp salt is cheap enough it is used instead of common salt, as its percentage of soda (8 to 12 per cent.), is made available, and the sodium chloride in it costs little or nothing.

Strength of Ash.—Soda ash is always sold according to its strength, as shown by test acid, and it is mostly only tested in this way; only exceptionally, moisture, caustic, insoluble, &c., are estimated as well. The test acid (usually standard sulphuric acid) saturates not only sodium carbonate, but also hydrate, silicate,

and aluminate; but all these together are classified as "available soda," and properly so, as for most purposes they are just as good as sodium carbonate. The test is expressed professedly in percentages of sodium oxide (Na_2O), and accordingly chemically pure sodium carbonate ought to test = 58·49, or, say, 58½ degrees. It is, however, not usual in this country to certify the strength of soda ash according to its real equivalent of 23 for Na, or 106 for Na_2CO_3; but according to an assumed equivalent of 24 for Na, or 108 for Na_2CO_3, called the "old" equivalent. The figures in Pattinson's table (given below), called "English degrees," are calculated on this basis, according to which pure sodium carbonate tests 59·26 per cent. The tests made in Newcastle, London, and Glasgow agree with this; but the "Liverpool" test, which does not seem to follow certain rules, shows about 1 per cent more. Another source of error is frequently imported by not filtering the solution of soda ash before testing it. The calcium carbonate and ferric oxide thus count equally with the available soda, and makes it appear a half per cent, and often more than that, too high; this custom is, however, not an acknowledged one, and certainly seems very reprehensible. In Germany soda ash is sold by its percentage of sodium carbonate (all "available soda" being calculated as such), and in France by Decroizilles' degrees. The latter are supposed to show how much sulphuric monohydrate (H_2SO_4, equivalent 98) corresponds to the percentage of Na_2CO_3 (equivalent 106); pure sodium carbonate accordingly tests 92·45° Decroizilles. The following table, composed by John Pattinson, will be found very useful for a comparison of the different degrees used by English, German, and French chemists, with the real percentages of soda:—

ALKALIMETRICAL TABLE.

Percentage of Soda.	Carbonate of Soda.	English Degrees.	Decroizilles' Degrees.	Percentage of Soda.	Carbonate of Soda.	English Degrees.	Decroizilles' Degrees.	Percentage of Soda.	Carbonate of Soda.	English Degrees.	Decroizilles' Degrees.
30·0	51·29	30·39	47·42	46·0	78·66	46·60	72·71	62 0	106·01	62·82	98·00
30·5	52·14	30·90	48·21	46·5	79·51	47·11	73·50	62·5	106·86	63 32	98 79
31·0	53·00	31·41	49·00	47·0	80·37	47·62	74·29	63·0	107·72	63·83	99·58
31·5	53·85	31·91	49·79	47·5	81·22	48·12	75·08	63·5	108·57	64·33	100·37
32·0	54·71	32·42	50·58	48·0	82·07	48·63	75·87	64·0	109·43	64·84	101·16
32·5	55·56	32·92	51·37	48·5	82·93	49·14	76·66	64·5	110·28	65·35	101·95
33·0	56·42	33·43	52·16	49·0	83·78	49·64	77·45	65·0	111·14	65·85	102·74
33·5	57·27	33·94	52·95	49·5	84·64	50·15	78·24	65·5	111·99	66·36	103·53
34·0	58·13	34·44	53·74	50·0	85·48	50·66	79·03	66·0	112·85	66·87	104·32
34·5	58·98	34·95	54·53	50·5	86·34	51·16	79·82	66·5	113·70	67·37	105·11
35·0	59·84	35·46	55·32	51·0	87·19	51·67	80 61	67·0	114·56	67·88	105·90
35·5	60·69	35·96	56·11	51·5	88·05	52·18	81·40	67·5	115·41	68·39	106·69
36 0	61·55	36·47	56·90	52·0	88·90	52·68	82·19	68·0	116 27	68·89	107·48
36·5	62·40	36·98	57·69	52·5	89·76	53·19	82·98	68·5	117 12	69·40	108·27
37·0	63·26	37·48	58·48	53·0	90·61	53·70	83·77	69·0	117·98	69·91	109·06
37·5	64·11	37·99	59·27	53·5	91·47	54·20	84·56	69·5	118·83	70·41	109·85
38·0	64·97	38·50	60·06	54 0	92·32	54·71	85·35	70·0	119·69	70·92	110·64
38·5	65·82	39·00	60·85	54·5	93·18	55·22	86·14	70·5	120·53	71·43	111·43
39·0	66·68	39·51	61·64	55·0	94·03	55·72	86·93	71·0	121·39	71·93	112·23
39·5	67·53	40 02	62·43	55·5	94·89	56·23	87·72	71·5	122·24	72·44	113·02
40·0	68·39	40 52	63·22	56·0	95·74	56·74	88·52	72·0	123·10	72·95	113 81
40·5	69·24	41·03	64·01	56·5	96·60	57·24	89·31	72·5	123·95	73·45	114·60
41·0	70·10	41·54	64·81	57·0	97·45	57·75	90·10	73·0	124·81	73·96	115·39
41·5	70·95	42·04	65·60	57·5	98·31	58·26	90·89	73·5	125·66	74·47	116·18
42·0	71·81	42·55	66·39	58·0	99·16	58 76	91·68	74·0	126·52	74·97	116·97
42·5	72·66	43·06	67·18	58·5	100·02	59·27	92·47	74·5	127·37	75·48	117·76
43·0	73·52	43·57	67·97	59·0	100·87	59·77	93·26	75·0	128 23	75·99	118·55
43·5	74·37	44·07	68·76	59·5	101·73	60·28	94·05	75·5	129·08	76·49	119·34
44·0	75·23	44·58	69·55	60·0	102·58	60·79	94·84	76·0	129·94	77·00	120·13
44·5	76·08	45·08	70·34	60·5	103·44	61·30	95·63	76·5	130·79	77·51	120 92
45·0	76·95	45·59	71 13	61 0	104·30	61·80	96·42	77·0	131·65	78·01	121·71
45·5	77·80	46·10	71·92	61·5	105·15	62·31	97 21	77·5	132·50	78·52	122·50

The first column contains percentages of soda, calculated on the correct atomic weight—31. These also represent what are known in France as Gay-Lussac's Degrees.

The second column contains the amounts of carbonate of soda corresponding to the soda in the first column. Soda ash is sold in Germany, Russia, &c., by the percentage of carbonate of soda it contains.

The third column gives the corresponding percentages of soda according to the English test, which is based on the old atomic weight of soda, 32, still retained as a trade custom in England.

The fourth column shows the corresponding degrees of Decroizilles' Alkalimeter. These degrees represent the number of parts of monohydrated sulphuric acid (oil of vitriol) which can be neutralized by 100 parts of the sample under examination. Decroizilles' degrees are used in France and some other parts of the Continent.

Note.—In the commercial testing of samples of soda ash and alkali, all the soda neutralized by test acid is taken into account, and reckoned as soda in the mode of stating the results shown in the first and third columns, as carbonate of soda, as shown in the second column, and as degrees, as shown in the fourth column.

Loss of Soda in Leblanc's Process.—This constantly occurs from a variety of causes, which are mainly the following:—1. Incomplete conversion of sodium chloride into sulphate. 2. Incomplete decomposition of sodium sulphate in the ball-furnace, and re-formation of the same in the lixiviating tanks, &c. 3. Mechanical carrying away of sodium salts into the flues. 4. Volatilization of sodium salts as such, or as reduced sodium (this source of loss has been proved to be of the most insignificant character). 5. Formation of sodium salts, which later on do not form the "available" soda, such as sulphide,

cyanide, sulphocyanide, ferrocyanide. 6. Formation of insoluble sodium compounds, partly as ferro-sodium sulphide, and partly as composite silicates in combination with lime, magnesia, alumina, &c. 7. Incomplete lixiviation. 8. Mechanical losses by leakages of liquors and scattering of salt and ash during the operations. The total loss from all these causes amounts to 14 to 20 per cent. of the total. It is considered very good work if a yield of 75 parts of soda ash, calculated as 48 per cent., from 100 parts of sulphate, is obtained; this corresponds to 69·23 per cent. of 52 per cent. ash, or to 60·15 per cent. of pure Na_2CO_3 on 96 per cent. sulphate = 62·66 on pure Na_2SO_3. The yield in German works is stated = 64 per cent. pure carbonate from 100 pure sulphate, instead of the theoretical 74·6—probably a maximum figure. The loss under the head **No. 6** (by the formation of insoluble compounds) has been carefully investigated by Scheurer-Kestner, who has shown that it increases with the quantity of limestone or chalk used in the ball-mixture, and this is a strong reason why the proportion of chalk should be kept as low as consistent with a complete decomposition of the sulphate. The loss from this source alone may amount to 5 per cent. of the available soda.

Refined Alkali.—The ordinary soda ash (yellow carbonate) is sufficient for most purposes to which sodium carbonate is applied in the arts. In most cases it has to be dissolved in water before use, by which process its insoluble impurities at any rate are removed; but this is not the case where the ash is used without dissolving, as in glassmaking and in a few other cases. There is, therefore, a constant demand for a purer article than the ordinary yellow carbonate, and a certain portion of the latter is consequently further refined. The usual refining process removes the insoluble impurities, as well as all sulphur compounds below sulphate, and all iron; but it does not diminish the proportion of chloride and sulphate in the ash. Where these are injurious (as in flint-glass making), a different article must be used, such as fished ash, or calcined crystals, or ash made by the ammonia process. The ordinary refining process for 50 or 52 per cent. alkali is carried out as follows:—Ordinary soda ash (unground) is dissolved in water heated by steam, generally in a cylindrical vessel 8 to 10 feet in diameter, and about 6 feet high, provided with a central revolving shaft with arms for agitating the liquid (see Figs. 29, 30. When the ash has been very well carbonated, nothing further is needed; but in the contrary case a small quantity of bleaching powder is put in the dissolver before running it off, and the boiling is continued for a quarter of an hour. The colour of the solution, which should be perfectly bright and as clear as water, generally decides upon that point. In no case ought more than 6 or 8 lbs. of bleaching powder per ton of ash be used. The bleaching powder (chloride of lime) thoroughly destroys any remains of organic substance (ulmates); it further oxidises the sulphite and the sulphide (if any) to sulphate, and the iron protosalts to persalts, from which the iron is at once precipitated as ferric oxide, and carried down with the calcium carbonate formed by the action of the chloride of lime on the sodium carbonate. The clear solution now contains nothing but sodium carbonate, chloride, and sulphate and hydrate; the silicate and aluminate generally also go unchanged through the operation. As the chloride of lime destroys a corresponding portion of sodium carbonate, it is evident that no more of it must be used than is absolutely necessary for the purpose in question. Whenever it is employed the resulting refined alkali, in spite of its containing an insoluble residue, shows a slightly lower alkalimetrical test

Fig. 29.

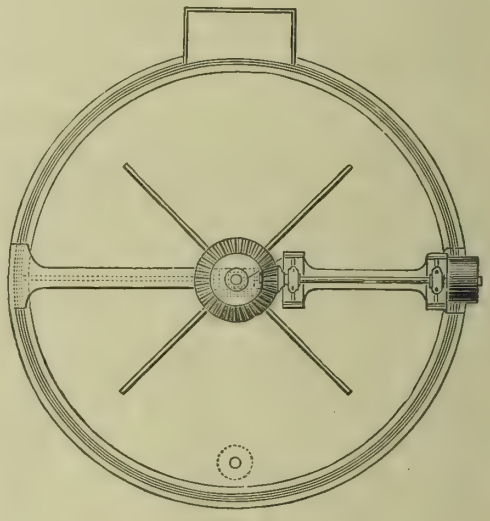
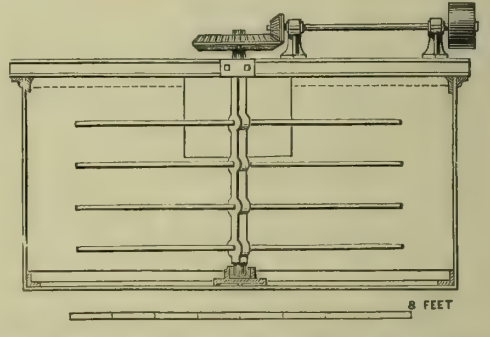


Fig. 30.



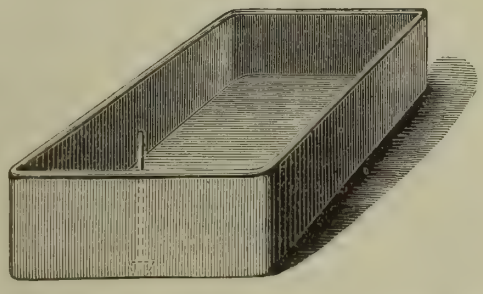
than the soda ash from which it has been made. The solution is now run off, along with all precipitates, into settling tanks; very much indeed depends upon the settling being done properly and completely, and it is best not to trust to one settling tank, but to employ two or even three. It is a good plan to make them very long, and to let the solution pass in at one end and out at the other. At the same time the liquor must not be allowed to remain so long in the settlers that it can crystallize; the original solution should not be made stronger than 56° Tw. (= 1·28 specific gravity), to provide against this contingency. Fortunately, as is well known,

the solubility of sodium carbonate (and sulphate) in water does not increase regularly with the temperature, but is highest at 38° C., so that no crystallization can take place whilst the boiling hot solution cools down to this temperature. But it is always best to surround the settlers with a bad conductor for heat (bricks, wood, &c.) The completely settled and clear solution is now evaporated in an open pan, covered by an arch, by surface heat; the construction of the pan itself and of its drainer is exactly like that of the common open black-salt pan as shown on the Plates, except that the white-salt pans are generally onger (up to 30 feet), and provided with a fire-place at each end, the flame escaping through a flue built in the arch in the centre of the length of the pan. The reason for this is to avoid the formation of smoke as much as possible, which, experience shows, cannot be avoided with a single fire at one end even when only coke is used as fuel, as is generally the case. The liquor is boiled down to a paste, the pans emptied into the drainer, and the drained white salt furnaced in a furnace exactly like a carbonating furnace, but of course with much greater ease than in the ordinary carbonating operation. It is not usual (as stated in text-books) to employ the waste heat of the finishing furnace (white ash furnace) for evaporating the liquor; it is nothing like sufficient for this purpose, and separate fires must be provided, which moreover allows the use of coals in the furnace, whilst coke is used for boiling down. The refining operation causes a loss of about 5 per cent. of the weight of soda ash originally employed. The refined alkali is ground and packed exactly like ordinary ash. The mud remaining in the settlers is washed with hot water; the washings are used for dissolving fresh soda ash, and the residue is thrown away. This operation is rather troublesome, as the mud is of a slimy character and difficult to wash; it is, therefore, sometimes put back among the balls into the lixiviating tanks. In large works it might pay to put it on a bed of porous bricks, and exhaust the air underneath to quicken the filtration, similar to the operation in caustic soda making.

Soda Crystals.—For some purposes even purer sodium carbonate is required than furnished by the refined alkali of trade, and formerly (before the perfection of fishing and the introduction of the ammonia process) the only available method for obtaining this on a large scale was by the manufacture of crystallized soda. This compound ($Na_2CO_3 + 10H_2O$) contains 63 per cent. water, all of which has to pay the same freight as the 37 per cent. sodium carbonate, and indeed much more, inasmuch as soda crystals are much bulkier than soda ash, and the freight for them is consequently higher, weight for weight, than that of soda ash. It would therefore seem to be quite out of the question to manufacture large quantities of this article, as its greater purity in comparison to that of soda ash or refined alkali is only very rarely a sufficient consideration for the extra cost and freight. And yet, for all that, soda crystals are manufactured on a colossal scale both in this country and abroad; indeed, many factories abroad do nothing but buy English soda ash and make it into crystals. The explanation of this apparently strange fact is this—that the large proportion of water which is a drawback for most commercial applications, is of great value for the domestic use of soda in washing and other household operations. The large bulk of the enormous quantities of crystals manufactured is ultimately used for such purposes. The crystals are more easily divided in small portions without soiling cupboards, &c., and they do not act so strongly upon the hands of the washerwomen and cooks who use them as the ordinary calcined alkali would do.

The manufacture of soda crystals seems easy; but it is nevertheless an operation requiring some care, as it is out of the question to crystallize more than once, and the crystals must be both of good colour and shape from the first. To begin with, the soda ash used for this purpose must be as well carbonated as possible. It does not matter in the least how yellow (from ferric oxide) it is, so long as it is free from sulphides and moderately so from caustic. Whilst bleachers, papermakers, soapmakers, &c., rather like some percentage of caustic in the ash, crystalmakers insist upon getting no more than 1 to 1½ per cent. of caustic in their ash. Any larger proportion both spoils the colour of the crystals (by its action on ulmates and other organic compounds) and causes a loss in crystallizing, since caustic soda, of course, does not crystallize, but remains in the mother liquors. The operations of dissolving and settling are exactly like those in making refined alkali, which have been described above. The solution, after having been bleached (if necessary) and completely settled, is run into coolers, generally made of cast iron, and known in the factories as "cones" (from their original shape), and allowed to stand for a week or ten days, according to the season, in order to crystallize. The cones are very frequently made in the shape of circular pans, about 9 feet in diameter and 3 feet deep; but a more convenient shape is shown in the woodcut, viz., a rectangular pan with rounded corners (Fig. 31),

Fig. 31.



with the bottom sloping to one side, and with a plug-hole and plug at this low end. Whilst in the ordinary circular cones the mother liquor has to be partly siphoned and partly baled off, it runs away by itself from the cones just described after the plug has been loosened, and the crystals drain mor

completely in the cone than in the old system. There is, of course, a system of spouts (mostly cast-iron ones) arranged over the cones, of which sometimes several hundreds are placed in one shed, in order to feed them with hot liquor; and another system of spouts is laid in the ground, mostly level with it, in order to carry away the mother liquor. There are always strips of hoop iron laid over the cones, slightly hanging down into them, so that they are covered by the liquor in filling the cones; they are laid crossways, and form a support for the formation of a crust, which soon covers the whole surface of the cone, and ultimately becomes quite a foot thick. This crystal is generally the very best and whitest. That attached to the sides and bottom is also broken off in as large lumps as practicable, and laid on a wooden bench to dry superficially for twenty-four hours. It is then, still somewhat wet, packed into the casks, the interstices between the larger lumps being skilfully filled up with the smaller fragments always occurring. It is sent out in casks holding from 2 to 8 cwts., and the custom on the Tyne is not to tare the casks at all, but to invoice the gross weight of the casks. The buyers, of course, are aware of this, and generally assume that 7½ per cent. of the weight invoiced is not soda, but the tare of the casks. Each cone of the former shape yields about a ton, and those of the rectangular shape about 28 cwts. of soda crystals.

The French market requires a whiter and drier kind of crystal than the English one, and their mode of operation is rather different from that used in this country. The crystallizing cones are very small—sometimes round, sometimes square, and tapering to the bottom—about 18 inches wide and 9 inches deep. They are mounted on wooden frames in three or four tiers, one over the other. After standing forty-eight hours (in summer this operation is not carried out at all in France), they are lifted off the stand, which can be done by one man; the mother liquor is poured off, and the cone is placed in a pan filled with boiling water, which, however, does not run into the cone itself. After a few moments the small cone is lifted out again; and as that portion of crystals immediately adhering to its sides has been melted by the heat, the whole of the crystallized contents can be tilted out as one block. These blocks are placed on edge on wooden racks, standing, one leaning against the other; and when completely drained, are transferred to a drying chamber heated to about 30° C., where they remain till they are quite dry, but not till they begin to effloresce. This kind of work requires more labour than the English style, but the result is better.

The mother liquors from the crystallizing cones are concentrated in an iron pan up to the salting point, and furnaced exactly like white alkali. They yield a very white product, called mother alkali, which in winter, when the crystallization is very good, only shows 30 per cent. alkalimetrical test; but in summer the test comes up to 40 and sometimes even to 44 degrees, which of course means a corresponding loss of crystals. The low strength of this mother alkali is caused by its large percentage of sodium sulphate, which almost entirely remains in the mother liquors; and it is therefore in good request by glass-makers, who only pay for the alkalimetrical test, but to whom the sodium sulphate, which they get for nothing, is almost equally valuable.

SODIUM BICARBONATE.—*Bicarbonate of Soda, Hydrogen and Sodium carbonate, Hydrosodic carbonate, Monosodic carbonate, Acid sodium carbonate*—$NaHCO_3$. This salt may be obtained by passing carbonic acid through a concentrated solution of the neutral carbonate, or by placing crystals of sodium carbonate in an atmosphere of the gas. In both cases bicarbonate of soda separates after a time in minute crystalline grains.

SCHÖFFER'S process was to mix 1 part of commercial sesquicarbonate of ammonia (chiefly bicarbonate) with 3 to 4 parts of crystallized sodium carbonate. The semi-fluid mass thus obtained on being heated gives off ammonia, and sodium bicarbonate remains.

Sodium bicarbonate is slightly alkaline, reddens litmus, and has a feebly alkaline taste. At a moderate heat it loses half its carbonic acid and the whole of its water, and is reduced to the state of neutral carbonate. When the solution is heated to 70° C. carbonic acid is evolved.

Water at 10° C. dissolves about one-tenth of its weight of sodium bicarbonate; the solution evolves carbonic acid, if the temperature is increased to 70° C. the gas is given off rapidly, and at the boiling point the salt is reduced to neutral carbonate.

The process commonly followed for manufacturing bicarbonate of soda was suggested by SCHÖFFER. As the utilization of all the muriatic acid is very desirable, this salt is made in several alkali works where soda crystals are manufactured, and where, at the same time, there is a considerable quantity of weak hydrochloric acid produced, of insufficient strength to serve for the manufacture of bleaching powder. The acid is allowed to act upon limestone or chalk (of which the poorest kinds are available for this purpose) in large stone cisterns, laid in clay and well bedded. These are provided with a man-hole, with an inlet-pipe for the acid, which reaches nearly to the bottom on one side of the tank, with an overflow-pipe for the calcium chloride solution, and with an outlet-pipe for the gas. The man-hole serves for introducing the limestone, and for the occasionally cleansing of the cistern. The weak hydrochloric acid, which generally comes direct from the condensers, enters of course near the bottom of the cistern, where it at once disengages carbonic acid; and its supply is so regulated that it is completely saturated whilst rising in the cistern, as it is displaced by the fresh acid flowing in underneath, and thus the calcium chloride solution overflowing at the top is almost or quite neutral. The gas as it is evolved from the cisterns is often washed in a convenient apparatus, and then conveyed in pipes to the boxes containing the soda crystals. These boxes are mostly made of iron, and in various shapes,

frequently in the shape of a tent or a waggon boiler. Sometimes they are built of bricks. In any case, they are provided with a false bottom of laths or shelves, on which the soda crystals are piled up to the roof of the box, in lumps of about a foot square, and of such thickness as they come out of the crystallizing cones. Only the inferior crystal is generally used in the bicarbonate chambers, as both its chemical impurity and its slightly yellowish colour do not prevent it from making perfectly pure bicarbonate. The carbonic acid is very quickly absorbed; and as the resulting $NaHCO_3$ crystallizes without any water, 9 of the 10 equivalents of the water of crystallization, combined with sodium carbonate, become disengaged, and water collects at the bottom below the shelves, from whence it is generally conveyed away by an U-shaped tube, whose bend forms a trap for the gas. This liquor has in solution a certain amount of sodium bicarbonate or bicarbonate, along with practically all the foreign salts (sodium chloride and sulphate), whose proportion in crystal soda is, however, only slight, and which are much more soluble than bicarbonate. This mother liquor is either added to the tank liquor, which it helps to carbonate, or boiled down by itself, and made into weak alkali (of about 36 per cent. available soda).

The time requisite for completely converting the sodium carbonate into sodium bicarbonate varies very much, according to the size of the chambers, and indeed in the same chamber it is not equal; as a rule, the operation lasts from eight to ten days. The bicarbonate chambers are always provided with a charging door and a vent for the air; they are also generally connected in such a way that the gas entering into one passes through a second, and even a third chamber, to be fully utilized. Openings are provided, generally plugged up, through which the workmen try from time to time whether the operation is completed by thrusting iron rods into the mass; when they can do so without feeling the resistance of unconverted soda crystals, the process is considered complete. Other marks for it are the ceasing of the flow of liquor, and testing of a sample from the centre of the lumps with mercuric chloride, which must not form a yellow precipitate, but only a white cloud. During its progress considerable heat is evolved; and as this is prejudicial to the formation of bicarbonate, iron chambers are preferable to those made of brickwork. The bicarbonate, when the door is opened, still shows the shape of the crystals from which it has been made; but, instead of being transparent, they are perfectly opaque, and have the colour and other appearances of snow. As the salt comes out, it is still very damp; and it requires drying at a gentle heat, not exceeding 45° C. It is piled up in large stoves, sometimes 20 feet square, and exposed to the above-mentioned temperature for eight or ten days, by means of iron pipes heated by a hot-air apparatus, or by any convenient apparatus. Lastly, it is ground to an impalpable powder in mills entirely resembling ordinary flour mills. Great care is required in this operation, as any heating of the stuff in the mill would injure it by causing a loss of carbonic acid. After grinding, the powder is sifted through a cylinder sieve covered with brass-wire gauze of 360 meshes per square inch, and packed in small barrels of 1 cwt. each. Attempts have been made to dry it at ordinary temperature, by piling the damp bicarbonate on a large number of shelves in very thin layers, and connecting the whole system at one end with the atmosphere, at the other end with the chimney. This process is, however, too slow.

The yield of bicarbonate from fresh soda crystals is about 50 per cent. When the crystals are effloresced it is, of course, larger. Such effloresced crystals also absorb the carbonic acid much more rapidly than those containing the full amount of water of crystallization. Mohr has proposed to avoid the formation of mother liquor completely, and hasten at the same time the absorption of the gas, by mixing 1 part of crystallized with 3 of calcined soda, as this mixture contains just enough water to supply the hydrogen in $NaHCO_3$; but this process is never practised now on a large scale, because the calcined soda ash, or even refined alkali, is too impure and does not yield sufficiently good bicarbonate. Moreover, the absorption of carbonic acid is in that case too rapid, and the heating caused in consequence of this may spoil the product. Other sources of carbonic acid than that above described have also been proposed, such as that escaping in nature in some places from volcanic rocks, that evolved in alcoholic fermentation, and that produced in lime burning. The two former can only have quite local applications, and the latter is too troublesome to purify and cool sufficiently for the purpose.

The bicarbonate of commerce, as it is made in alkali works and principally used as baking powder, is never quite free from sesquicarbonate; but it ought not to be more than 2 per cent. short of the quantity of carbonic acid pure bicarbonate contains (52·38 per cent.). If 1·91 grams. are weighed into the carbonic acid apparatus, each ·01 loss of weight shows 1 per cent. of pure $NaHCO_3$.

Sodium Hydrate.—*Caustic soda*, *Hydrated oxide of sodium*, *Sodium hydroxide*—NaHO. This body is produced by adding water to sodium monoxide ($Na_2O + H_2O = 2NaHO$), or by decomposing a solution of sodium carbonate by calcium hydroxide. The clear solution is decanted from the precipitate and evaporated to dryness. This latter reaction is adopted in manufacturing caustic soda on a large scale.

Hydrate of sodium is a white, opaque, brittle substance, of a fibrous texture; it fuses below redness. In properties it greatly resembles the corresponding potassium hydroxide, but is less volatile at a red heat. Specific gravity 2·00.

When exposed to the air it rapidly attracts moisture, becomes liquid, but soon dries up again by absorption of carbonic acid, the mass becoming converted into carbonate, which is not deliquescent.

A solution of sodium hydrate dissolves wood,

hair, the skin, and most animal substances, sulphur, and some metallic sulphides, silica, alumina, and some metallic oxides which are quite insoluble in water.

The oldest method of making caustic soda is due to Scheele; it consists in the decomposition of sodium chloride by litharge. This method was employed in England for producing, besides caustic soda, the fine pigment known as *Patent yellow*. The operation consisted in intimately mixing and rubbing together 1 part of salt, and from 4 to 6 parts of litharge with a little water.

About twenty-four hours are required to complete the decomposition, during which time the mixture must be constantly agitated. It is then allowed to stand a few hours to settle, and the caustic soda solution is then decanted, and the residue well washed with water. The decanted solution on evaporation yields very pure sodium hydrate, and the lead compound, after being dried and fused, becomes of a beautiful yellow colour.

The history of this very important branch of alkali manufacturing is a very short one, as far as the production of solid caustic is concerned, though this is now practised on an enormous scale in Lancashire, and to some extent also on the Tyne. It seems to have occurred to Gossage before anybody else (in 1853) to adopt an operation opposite to that of carbonating the caustic in tank liquors, viz. — to separate the carbonate (along with other sodium salts) from the liquors by concentration and fishing out, and to leave the hydrate in solution as red liquor, from which by further concentration solid caustic could be produced. The first article thus produced was of a very inferior colour, owing to the presence of iron sulphide and oxide in considerable quantities; but very soon improvements upon this were patented by Stott (1855) and Gossage (1857), whose object was the removal of the sulphides. In 1857 Bakewell introduced the packing of caustic in iron drums, which is now the usual way.

About this time manufacturers, finding the demand for caustic to exceed the supply, also began to causticize tank liquor direct by lime; and as the great dilution of the liquors caused the expense of concentration to be very high, Dale (in 1859) patented the process of concentrating the weak caustic liquors in steam boilers, and using the steam for various purposes. The next real improvement was made in 1860 by Ralston, who prescribed, in lieu of keeping the heat as low as it had been formerly usual, to work at a greater heat, and to continue the evaporation till the iron separates as ferric oxide, and is precipitated at the bottom of the vessel; the clear caustic floating over it to be separated from the bottoms. This process for the first time allowed of the manufacture of *white* caustic, before this only *cream* caustic could be produced; and at the same time a stronger article (70 per cent.) could be produced in the place of 60 per cent. caustic, which was up to that time the only practicable strength. This was, however, only possible by employing much stronger melting pots than were used up to that time. For several years not much white caustic was made; but in 1872 Pauli published the process which is now the only one in practical use, and which will be described hereafter. Its main feature was to heat commercial caustic to fusion and keep it at that temperature through the night, when, besides the oxide of iron, the alumina is separated as a crystalline silicate. About the same time Deacon patented a process for producing crystals of caustic soda, by evaporating until the boiling temperature is 177° C., cooling down to 70°, and running off into cast-iron cones for crystallization; a hydrate of the following composition crystallizes out:—

Sodium oxide,	50·5
Sodium hyposulphite,	0·5
Sodium chloride,	1·8
Water,	47·2

The cones must be kept warm, and when their contents have cooled down to 50°, the mothers are run off through a plug hole in the bottom; the cones are then heated by steam outside, which melts the crystals inside so that they can be ladled off into the drums. This process has, however, never been a commercial success. The demand for caustic becoming stronger, some works, principally on the Tyne, actually began to make it by redissolving ordinary soda ash, causticizing it by lime, and evaporating the lyes; and this extremely costly and irrational process has been in use for many years, and may be so yet here and there. The great bulk of the caustic soda found in commerce is made at Widnes, where one firm turns out equivalent to 250 tons of 60 per cent. caustic per week, and several others from 60 to 80 tons each, and at St. Helens, where there are four or five works of the same size. Most of this (not all, as stated by Davies, to whose paper on white caustic soda the writer is indebted for most of the above historical data, as well as for a great portion of the following description) is made by causticizing vat liquors by lime, whilst a small portion of white and most of the cream caustic is made from the red liquors. Wagner's statement in his "Technology" (English edition of 1873), that "the use of lime for the transformation of sodium carbonate into caustic soda has been abandoned long since," is therefore quite erroneous.

Where caustic is made, the mixture for the balls is now regularly partly compounded with the lime mud from the causticizers, and with the fished salts separating at various stages of the concentration of the causticized liquors. The following are ball mixtures given by Davies from actual experience:—

Sulphate of soda,	2½ cwts.
Lime mud,	2½ "
Limestone,	1½ "
Coals,	1½ "
Fished salts,	14 "

Sulphate of soda,	2½ cwts.
Lime mud,	5 "
Coals,	1½ "

Fished salts,	2 cwts.
Limestone,	3 "
Coals,	1½ "

The two last-mentioned mixtures, however, are quite exceptional, and ought not to be used, but rather the first compounded mixture.

There is no difference whatever in the lixiviation from that practised for soda ash; but of course the carbonating process is never performed, instead of which sometimes the oxidising by air, mostly by HARGREAVES' blower, is carried out. This is, however, quite unnecessary as a special process, since it can be combined with the causticizing, as will be shown presently. The tank liquor is, therefore, nearly always pumped or run direct from the liquor settlers into the causticizing vessels (operation pans). These are always of iron (cast, or mostly wrought), but of no definite shape; frequently old boilers cut in halves are employed for this purpose. When the agitation takes place by a mechanical stirrer, circular vessels are often preferred, but not always even then. In this case a small bracket engine is bolted to the pan, which is, moreover, provided with one or more steam-pipes for heating the charge, a sludge valve for the mud, and a drop siphon for removing the clear liquor, except when the whole of the charge is run out at once. Small causticizers can be worked without an engine, the agitation produced by the blowing in of steam being sufficient; but the best system of all is to produce the agitation of the mud and liquor by means of a "blower" worked by a steam jet, of which that constructed by KOERTING BROTHERS is the most economical in working. This last method possesses the very great advantage that the mixture of air and steam, which serves for agitation, at the same time heats the liquor, and lastly, oxidises the sulphides, so that the preliminary oxidation can be dispensed with, as above mentioned.

The tank liquor (which ought to be well settled for making *white* caustic) is always diluted with hot water, but not always to the same degree. The minimum strength found in practice is 15° Tw., the maximum 20° Tw., but most factories work at 16° to 18° Tw. DAVIES has proved that a liquor of 20° Tw. can be quite as thoroughly causticized as one of lower strength; and although it takes naturally a little more time, there is not only more work done, but there is much less water to evaporate. When the total has been brought to the boil by injection of steam, quicklime is put into the cage, and the steaming and agitation is carried on until the contents of the pan are thoroughly causticized. An experienced workman can tell pretty nearly, by the kind of boiling, the colour, and other indications, when the liquor is completely causticized; but a test is always made by taking out a sample, settling or filtering it, and trying the clear liquor for effervescence by addition of a little dilute sulphuric or hydrochloric acid. After this the whole is sometimes run off to a separate settling pan; it is, however, more usual to allow it to stand for half an hour, remove the clear liquor by means of a swivel or drop siphon, as nearly as possible into the caustic liquor settlers, and to run a fresh quantity of tank liquor upon the lime mud, which always contains some free lime, so that the second charge does not require quite so much lime as the first. When this second charge in its turn has been causticized, settled, and the clear liquor run off, the agitator is started again, fresh water is run on to the lime mud in the pan and steamed up with it; it is allowed to settle again, and the clear liquor is used for diluting the tank liquor of a further batch. The mud now remaining is stirred up with a little water and run on to the filters, where it is allowed to drain, either by itself, or by preference with the aid of a vacuum pump. The filter is also again a half-boiler, but when made on purpose, is something like 20 feet long, 10 feet wide, and 4 feet deep. On the bottom are placed bricks on edge 2 inches apart from each other, and leaving a clear channel in the centre, covered over with bricks or slabs. The whole arrangement is covered with 8 or 9 inches of limestone, or better, of coke, in pretty large pieces; over these another layer of smaller, and over this a third layer of still smaller pieces. Lastly, a layer of clean coarse sand or small coals, on which cast or wrought iron grids are laid to afford a smooth shovelling bottom. A few clean riddled cinders from one of the furnaces renders the filter, of which there still remains 18 to 24 inches of clear space, available for use; but communicating with the bottom channel above described there is an iron pipe (2 or 3 inches wide) connected with a small boiler or air-tight tank of about 150 to 200 cubic feet capacity, erected above the level of the causticizing pan, and connected in its turn with a vacuum pump. The top of this boiler is provided with an air-cock, and its bottom with a running-off cock for the collected water; it has also a water-gauge. As soon as this filter has received a batch of mud from the causticizing pans the vacuum pump is set in motion, and first the air and then, as rapidly as it collects, the filtrate is withdrawn from underneath the bed. Very soon cracks appear on the surface of the mud. These are immediately obliterated with a wooden rake, whilst a supply of water is run on and worked well into the mud to remove as much soda as possible. After three or four hours the magma has become very firm and all available liquor is got from it; the vacuum pump is now stopped, the liquor which is now in the receiving-vessel or boiler is run into the causticizing pan to assist in diluting a fresh portion of tank liquor, and the mud is shovelled out of the filter and wheeled to the ball-furnaces, where it is used as above mentioned (MORISON). Its composition as it goes into the ball-mixture is stated by DAVIES as follows:

	A.	B.
Calcium hydrate,	2·825	2·652
Sodium hydrate,	1·906	1·663
Sodium chloride and sulphate,	0·244	0·206
Calcium carbonate,	40·170	42·031
Calcium hydrate,	3·759	3·072
Silica,	0·673	0·774
Alumina,	0·255	0·324
Ferric oxide,	0·048	0·708
Magnesia,	0·086	0·095
Soda,	1·832	1·600
Water,	47·986	46·577
Total,	99·781	99·702

The first three items bracketed together were soluble when 5 grams. of the mud were digested in 100 c.c. of water at 100° C. No other use than that for the ball mixture has been found practicable for the lime mud, except where green glass works exist in the neighbourhood; it costs far too much to reconvert it into caustic lime.

As will be seen from the above analyses, the lime mud always contains a not inconsiderable quantity of soda, both in the soluble or insoluble state; but even the former cannot practically be got out on the large scale. Assuming it to amount to 1½ per cent. of available soda (Na_2O), the loss will be as follows:—For each ton of 60 per cent. caustic soda, about 11 cwts. of good lime are required; these yield about 36 cwts. mud, containing, at the rate of 1½ per cent., 60 lbs. of real soda, or equal to 100 lbs. of 60 per cent. caustic per 2240 lbs. of the same actually obtained. If weak lime be used, the loss is proportionally greater, as more mud is then produced. Whether any of the soda, even of its soluble portion, is actually recovered again by using the lime mud for the ball mixture, appears at present still a questionable matter.

The following are analyses, by Davies, of diluted tank liquor before causticizing (A), and of the same liquor after causticizing (B), the agitation of the operation having been produced by means of injection of air:—

	A.	B.
Iron sulphide,	traces.	none.
Iron oxide,	none.	traces.
Sodium sulphide,	1·068	none.
" sulphite,	0·151	0·264
" hyposulphite,	1·137	1·864
" sulphate,	5·423	5·006
" chloride,	8·576	7·995
" silicate,	0·852	0·176
" aluminate,	2·490	1·438
" carbonate,	53·167	2 954
" hydrate,	44·280	74·000
" ferrocyanide,	0·093	0·086
" sulphocyanide,	0·054	0·050
" phosphate,	traces.	traces.
Insoluble,	0·849	none.
Total solids per litre,	118·140	93·833

A had a specific gravity of 20° Tw. at 56° Fahr., and B 18° Tw. at the same temperature. It will be seen that the sulphides have been quite removed, and the silicate and aluminate greatly reduced in quantity.

The following is the composition of a liquor causticized at 15° Tw., the agitation being performed mechanically; the finished liquor showed 13° Tw.:—

Iron sulphide,	traces.
Sodium sulphide,	1·092
" hyposulphite,	1·264
" sulphite,	trace.
" sulphate,	3·264
" chloride,	4·212
" silicate,	0·151
" aluminate,	0·584
" carbonate,	7·844
" hydrate,	50·400
Other constituents,	0·200
Total solids per litre,	69·011

It will be seen that in this case the sodium sulphide still exists in the caustic. By blowing long enough, in the former kind of operation, all the lower compounds of sulphur may be converted into sulphate, but this is hardly ever attained in practice. The use of metallic oxides, of which many have been proposed for removing the sulphide from the liquor, is now made quite superfluous, as the oxidising is both much cheaper and easy of execution. The oxides of iron, zinc, and manganese have been tried, but had to be abandoned from practical reasons (sliminess of the metallic sulphides). Only lead oxide (litharge) has been found practicable; but its use seems quite unnecessary, since the same object can be attained much more cheaply by using a blower instead of a mechanical agitator in the causticizing or "operation" pans. Certainly when using litharge stronger caustic can be obtained than by any other method, as the sulphide is converted into caustic instead of into sulphate. At Dieuze (in Lorraine) lead sulphate is used for the same purpose.

The caustic liquor is allowed to settle in special tanks, and when perfectly "bright" is run off to the concentrating apparatus. This was thought at one time to be done most economically by Dale's process, in steam boilers, which thus produce the steam for causticizing free of cost; but this mode of concentration is now very little employed, as the boilers suffer very much, and any negligence on the part of the workmen might produce disastrous results. It would appear as if the sodium sulphide acted corrosively upon the iron, and therefore certainly only liquor freed from it by blowing or by litharge ought to be used in this case. Any approach to the salting point must be strictly avoided, and the strength of the liquor in the boilers ought never to be allowed to exceed 30° Tw., or 1·150 specific gravity, although J. Hofmann states that the liquids can be concentrated to 1·24 or 1·25 "without the slightest inconvenience." The evaporation of caustic liquors is, as well known, somewhat troublesome, in consequence of their liability to froth and boil over all at once; and this inconvenience, which in a steam boiler would be a very serious one, has been obviated by H. Deacon by placing within the boiler an inverted cast-iron funnel, resting against the sides of the boiler by a few points only. The vapour, as it forms, causes the liquid to froth up, and forces it inside the funnel to the top, where it pours over continually, and thus prevents the too violent ebullition of the liquid outside the funnel.

In any case, whether direct from the caustic settlers or from the steam boilers, the liquor is now concentrated in boat pans, of which there generally are two, placed end to end, so as to form a prolongation of the black-ash furnace, as it has been described in connection with the same. In some works a cast-iron pan is placed next to the furnace, and a wrought-iron one at the end of this, and the weak liquor for concentration is sometimes run into the front and sometimes (much more frequently) into the back pan first.

Other works use two wrought-iron, or, again, two cast-iron pans; and no fixed opinion seems to exist which of the two kinds of metal is preferable for "weak" pans—that is, such as are heated by waste furnace gases. The "strong" pans, however, which have to finish the boiling previous to the "pots" themselves, are nearly always of cast iron.

The pans for strong liquor have fires of their own—viz., two fire-places, about 4 feet 6 inches by 2 feet 3 inches, arched over, and built in front of the two flues which have been described previously as running underneath the pans, so that each flue has a separate fire. At the back of the pan the two unite in a common drop; but often the fire first passes underneath a second or even a third pan—at least in the case of cast-iron pans, which are always much shorter than wrought-iron ones. The caustic liquor in the back pan does not get up to ebullition completely, and only reaches about 28° Tw. In the front pan it gets up to 45° or 50° Tw., but even then no salts are deposited, and it is then run into the "strong" pans.

Some manufacturers, however, attain a greater strength in the "weak" pans, and consequently have to begin "fishing" the salts in the same. This must always be done from the strong pans, which are supplied by a constant feed from the weak ones; and when a specific gravity of 60° Tw. has been arrived at, in some works the addition of nitre is commenced with a few pounds. The evaporation is continued till the liquor reaches 70° to 72° Tw., if for 60 per cent. caustic, or 80° to 85°, if for 70°; then the fires are allowed to burn down, and the pans to cool for an hour or two; the clear liquor is then drawn off through a swivel pipe into shallow settlers, and the salts remaining on the pan-bottom are taken out and placed on a small drainer by means of a perforated shovel, from which, after thorough draining, they are removed for use in the black-ash furnaces. The strong pans are run off about once in twenty-four to thirty hours, and about five of them are necessary to make up one 10-ton pot of finished caustic soda.

In the settlers which feed the pots a small additional quantity of "salts" is deposited, but only sufficient to necessitate a weekly or fortnightly cleaning; if they are dispensed with altogether (which should not be done when absolute immunity from carbonates is desirable), the settling time in the strong pans must be increased to six or eight hours (Morison).

Davies recommends strongly, instead of using the hydrometer, whose indications are rather unreliable for such high degrees and temperatures, to use the thermometer for fixing the time of running off the liquors, since the boiling point rises continually with the concentration, and in this case 280° Fahr. give the limit for running off the strong pans when 60 per cent. caustic is to be made. He also recommends to run weak liquor on to the salts, which causes them to be more easily detached for fishing.

The following are analyses of fished salts:—

	Davies.		Morison.
	A.	B.	
Insoluble matter (chiefly FeS),	0·742	1·004	—
Sodium sulphide,	0·116	0·097	—
" hyposulphite,	0·274	0·718	—
" sulphite,	3·723	2·695	—
" chloride,	7·024	5·834	0·50
" sulphate,	22·773	26·432	29·00
" silicate,	traces.	traces.	—
" aluminate,	traces.	traces.	—
" carbonate,	21·559	24·218	39·00
" hydrate,	8·417	10·116	9·00
Water (by diff.),	35·372	28·886	17·00
Total,	100·000	100·000	—

The salts deposited in the settlers after running from the strong pans, and before running into the caustic pots (which operation is not always performed), are more the result of a real crystallization by cooling. The following are analyses by Davies of these salts:—

	A.	B.
Insoluble (mostly FeS),	1·143	0·867
Sodium sulphide,	traces.	0·077
" sulphite,	2·734	1·013
" hyposulphite,	0·316	0·146
" sulphate,	9·768	5·772
" chloride,	33·674	60·443
" silicate,	traces.	traces.
" aluminate,	traces.	traces.
" carbonate,	15·052	5·683
" hydrate,	13·440	10·773
Water,	19·873	15·226
Total,	100·000	100·000

These salts are more of a "sloppy" nature than those got out of the pan. They form in much smaller quantity.

It has been mentioned above that in some works sodium nitrate is added to the liquor in the boat pans, which is supposed to "throw down" the salts; but care must be taken to add less than necessary, as if, on the contrary, more than necessary be used, the excess will be lost by separation with the salts. If the liquors have been thoroughly oxidised during the operation of causticizing, no nitre is necessary at this stage. According to Pauli, as long as the boiling point of the liquid is between 138° and 143° C. (280° and 290° Fahr.) the sulphide is quietly oxidised to sulphate, with the formation of sodium nitrite; at 155° C. (311° Fahr.) ammonia is evolved with violent effervescence and in large quantities. Davies doubts the correctness of this statement, as according to him, *below* 280° Fahr. much ammonia is evolved and little sulphite is formed. His researches have led him to believe that the oxidation of sodium sulphide progresses through the gradual stages of hyposulphite, sulphite, and sulphate, the reactions being:—

(1) $2Na_2S + NaNO_3 + 3H_2O = Na_2S_2O_3 + 3NaHO + NH_3$.

(2) $2Na_2S_2O_3 + 3NaHO + NaNO_3 = 4Na_2SO_3 + NH_3$.

(3) $5Na_2SO_3 + 2NaNO_3 + H_2C = 5Na_2SO_4 + 2NaHO + N_2$.

The first reaction takes place at or about 280° Fahr., and the hyposulphite remains mostly in the liquor; the second commences about 305° Fahr., and the sodium sulphite then formed rises and floats on the top of the pots as a white scum. The limit of the third reaction cannot be so clearly indicated; but, at any rate, the evolution of ammonia stops at 360° Fahr., and nitrogen is evolved in its place. All these reactions occur only with an excess of nitre, and some secondary reactions also take place.

The settled liquor from the strong boat pans is now further concentrated in "pots" (Figs. 32, 33). These are circular pans, constructed to hold 10 tons of fin-

Fig. 32.

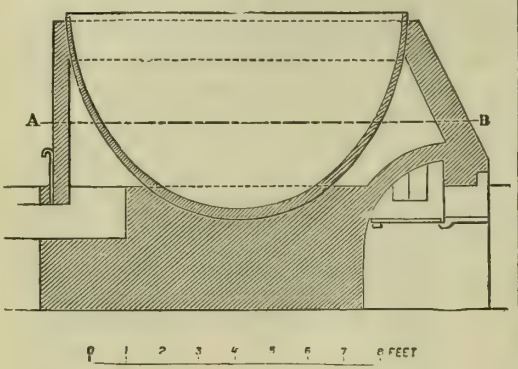
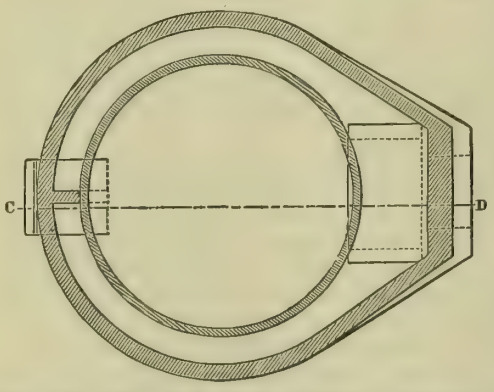


Fig. 33.



ished soda; they are 9 feet in diameter and 5 feet 6 inches in depth, and weigh about 6½ tons each. There is no fixed rule for setting them, but the common aim is always to divide the heat, so that the flame may play upon the pot all round; otherwise they would soon burn through in particular spots. The side of the pot against which the fire is built is nearly always protected from the direct action of the flame by a shield of brickwork, against which the flame splits in two portions, which play round the pot and unite again at its other side to pass into the flue. Generally the pots rest on a metal plate, and are stayed in an upright position with brickwork. The chief support is given by the circular wall surrounding it, and forming the side flues, into which three lugs, cast on to the pot in equal distances about a foot from the top, project. The metal plate just mentioned facilitates the turning of the pots, which is advisable to prevent them wearing too much in particular places, and the same object is assisted by an overhead travelling crane, which also greatly facilitates their putting in when new and removal when worn out. Sometimes pots are cast in two pieces, viz.—a lower semi-circular piece, and an annular piece bolted to the upper side of it; the latter lasts much longer than the former. Heating the pots by generator gas has been tried, but has been found to be uneconomical.

The liquor in the pots is kept boiling till a temperature of 320° Fahr. is reached. Beginning from 290° Fahr. a scum forms on the top, sometimes of a semi-transparent straw colour, sometimes red, and even black; at the same time the evolution of ammonia becomes very strong. This froth is sometimes not removed, when only 60 per cent. caustic is to be made; but when 70 per cent. has to be made, its removal is imperative. It is then taken off by means of a perforated scoop. Its composition seems to be the same whether nitre has been added in the boat pans or not, as shown by the following two analyses (by Davies), of which A refers to scum from a liquor boiled to 320° Fahr., oxidised during causticizing, but not nitred; whilst that in B had been nitred in the boat pans:—

	A.	B.
Iron peroxide,	traces.	traces.
Iron sulphide,	0·139	0·346
Sodium sulphite	51·408	57·120
" hyposulphite,	none.	traces.
" sulphate,	6·831	5·377
" chloride,	5·265	6·172
" silicate,	0·225	traces.
" aluminate,	traces.	traces.
" [illegible]onate,	15·408	13·013
" hydrate,	20·800	17·672
Total,	100·076	99·700

For the prepartion of 70 per cent. caustic there are still too many "salts" in the liquor, and to reach that strength with certainty it is best to allow the pot, after reaching 320° Fahr., to cool and settle again.

The following shows the composition of the settlings:—

Iron peroxide,	1·054
Sodium sulphite	3·603
" hyposulphite,	0·442
" sulphate,	1·146
" chloride,	41·535
" silicate,	0·174
" aluminate,	0·544
" carbonate,	11·488
" hydrate,	19·840
Water, (by diff.),	20·174

The boiling of the liquor is then continued, and when the temperature has reached 355°, it will solidify well on cooling, and contain 53 per cent. of alkali. At this stage the liquor is exceedingly apt to rise in the pot and boil over; this has to be kept down by the workmen beating down the scum, or by pouring in some oil. It is especially risky at this stage to run in any fresh liquor. When the temper-

ature has risen to 400° Fahr., very little steam seems to be evolved, although the contents of the pot still hold 20 per cent. water. At about 460° Fahr. the caustic contains as nearly as possible 60 per cent. alkali; at 470° Fahr., about 61 per cent.; and at 500° Fahr., about 64 per cent. About this time there is very little motion in the pot, and its temperature soon rises above the range of a mercurial thermometer.

At this stage some extremely pungent matter having a strong ammoniacal odour is thrown off, owing to the action of the caustic soda carried away by the steam, or perhaps by its action on the cyanides present.

The cyanides are destroyed with the formation of graphite (first observed by Dr. Pauli), which covers the surface of the pot.

Any boiling to be now observable is confined to a slight effervescent motion round the edges of the pot, and it soon ceases altogether. The pot is now covered with a sheet-iron lid provided with an opening at one side, and the fire is urged as strongly as possible.

The time has now arrived for the complete oxidation of the sulphur compounds. This can be done either by means of nitre, or by blowing in air. In the former case, the nitre is introduced (a hand scoopful at a time) through the opening in the lid. Its action is at first very energetic, often causing a deflagration. As the contents of the pot approach "clearness," the addition of nitre must be made with great caution, in order not to overdo it; every now and then a small sample is taken out, solidified on a clean shovel, and tried with a few drops of a solution of lead acetate. When this causes only a very faint darkening by transmitted light, the further addition of nitre is discontinued. From 40 to 45 lbs. of nitre suffice for 1 ton caustic in the case of good liquors.

The process of oxidation by means of a current of air was invented by Ralston, in 1860 and independently in 1865 by Peter Hart; it was again, without any essential modifications, patented in 1870 by Helbig, to whom in some German publications all the credit is given. The current of air is generated by an ordinary blowing engine with short stroke for low pressure. There must be a receiver with a safety valve for any water carried away from the blowing cylinders, if this, as usual, is lubricated by water, as in the pot it would produce an explosion. The engine usually adopted in Lancashire is double-acting, and if only intended for blowing two or three pots at a time, it has a 12-inch air cylinder and 12-inch stroke. The main delivery pipe has $2\frac{1}{2}$ inches, and is provided with a reducing tee for each pot and with a waste-cock. When a pot is ready for blowing, a strong $1\frac{1}{2}$ inch wrought-iron pipe, terminating at its lower end in a perforated ring of about 18 inches in diameter, or a tee of the same length, is plunged into the pot, till the ring or tee rests on the bottom; the upper end is joined by an india-rubber pipe and coupling screw to one of the branches of the air pipe. On starting the engine the waste-cock must be left open for a few seconds, to remove any water. The fused mass is soon in violent commotion, and after two or three hours becomes red hot. If the liquor has been good and the boat pans nitred, three to four hours blowing suffices; if no nitre has been employed in the pans, about eight hours. For inferior liquor much more (even thirty-six hours') blowing may be necessary. It must not be overdone any more than nitreing; but the caustic should become green by the formation of sodium manganate, and a trace of sulphide is therefore purposely left in. If the blowing (or nitreing) has been overdone, it is remedied by throwing in a small piece of sulphur or sodium hyposulphite. From 25,000 to 30,000 cubic feet of air are sufficient per ton of caustic. Nitreing occupies five or six hours, and about 10 per cent. less pot room is necessary for it than for the blowing, which causes a much more violent commotion. The reaction in this stage seems to be:—

$$5Na_2S + 8NaNO_3 = 5Na_2SO_4 + 4Na_2O + 8N.$$

After the oxidation a sample is withdrawn (which is always coloured brown or even red) and tested for its amount of total alkali. If intended for 60 per cent. caustic, the contents of the pot must now be reduced with common salt. It may turn out 68 to 70 per cent.; or if for 70 per cent. caustic, to 70 72 per cent. The addition of the salt must be made very cautiously, as it decrepitates on throwing it in, and causes an extremely irritating spray, and cools the pots, which must now be brought up to heat again, and allowed to stand for eight to twelve hours. The ferric oxide settles down to the bottom, along with sodium aluminate, and the fine quality of the caustic entirely depends upon the completeness of the settling; sometimes pots refuse to settle at all, especially when over-oxidised. The cause of the ferric oxide only settling down after the mass has been brought to igneous fusion is probably this, that it becomes much denser and heavier by ignition, as known to every tyro in analysis. The clear settled caustic is now baled out into the well-known circular sheet-iron drums, holding about 6 cwts. each, which are placed in two or more rows round the pot, and filled by a movable iron shoot. If quite perfect, the caustic ought to run down "as clear as gin." On approaching the lower part of the pot, the workman proceeds very cautiously; and as soon as the caustic becomes doubtful in quality, it is baled over into the next "strong" pot, till the workman comes to the "bottoms." These are either baled into separate drums, and sold as bottoms, or else into iron bogies, in order to be broken up, dissolved by help of steam to 48° Tw., thoroughly settled, and the clear liquor causticized. They amount to 9 to 11 per cent. in the caustic produced, and are generally sold as 54 per cent. strong; if stronger, they are reduced to this point by fished salts. The following are analyses of bottoms (by Davies)—A, from a pot very red before salting; B, from a pot whose liquors had been well oxidised in causticizing; C, from liquors only partially oxidised in causticizing:—

	A.	B.	C.
Insoluble matter,	23·000	1·948	4·664
Sodium hydrate,	58·888	70·896	71·866
" carbonate,	trace.	none.	0·722
" chloride,	6·135	14·040	10·729
" sulphide,	0·132	0·054	0·116
" sulphite,	0·151	0·063	0·074
" sulphate,	5·534	3·526	4·624
" silicate	0·683	trace.	trace.
" aluminate,	5·661	9·556	7·133
Total,	100·184	100·083	99·928

The following is the composition of the insoluble matter:—

	A.	B.
Graphite,	2·146	1·179
Ferric oxide,	93·000	94·006
Calcium oxide,	4·332	4·289
Manganese oxide and magnesium oxide,	0·522	0·526

ANALYSES OF WHITE 60 PER CENT. CAUSTIC.

	Davies.		Morison.	Glendinning, Tyne Caustic.
	A.	B.		
Sodium hydrate,	72·774	75·246	70·00	75·00
" carbonate,	1·419	2·536	6·00	1·50
" chloride,	18·800	17·400	18·50	9·80
" sulphate,	6·462	4·398	5·50	10·38
" sulphite,	0·063	0·027	—	0·80
" sulphide,	—	—	—	0·30
" silicate,	0·304	0·297	—	0·44
" aluminate,	trace.	trace.	—	0·31
Total,	99·822	99·904	100·00	98·53

WHITE 70 PER CENT. CAUSTIC.

	Davies.		Morison.
	A.	B.	
Sodium hydrate,	83·840	89·600	82·00
" carbonate,	4·686	2·481	5·00
" chloride,	6·522	3·919	7·00
" sulphate,	4·526	3·419	6·00
" sulphite,	0·025	0·025	—
" silicate,	0·463	0·304	—
" aluminate,	trace.	trace.	—
Total,	100·062	99·748	100·00

The caustic drums must be packed in three or four instalments, otherwise a hollow core is left in the centre, causing a loss in packing space. Glendinning and Edgar maintain that samples taken from different parts of a drum may show different percentages of alkali, but this is denied by Morison.

Caustic Soda from Red Liquors.—These (the mother liquors from the black-salt boat pans) generally stand at 62° Tw.; the following is an analysis by Davies:—

Iron sulphide,	0·313
Sodium bisulphide,	0·195
" sulphide,	6·256
" sulphite,	16·022
" hyposulphite,	7·858
" sulphate,	14·848
" chloride,	65·526
" silicate,	9·677
" aluminate,	1·031
" carbonate,	79·966
" hydrate,	194·400
" sulphocyanide,	0·261
" ferrocyanide,	0·423
Grams. per litre,	396·776

From these red liquors best white caustic is sometimes obtained, but as a rule this is not done, and only the article called "cream caustic" is worked for. Into its manufacture enter at the same time the dissolved bottoms spoken of, and sometimes tank liquor causticized in the usual manner. The red liquor, thoroughly settled, is boiled down in a self-fired boat pan (say 30 feet × 8 feet × 2 feet 6 inches), until it reaches 70° Tw., or a boiling point of 250° Fahr. The pan is then cooled down and thoroughly fished. It is then re-heated to boiling, and 2½ to 3 cwts. nitre added; and when, after continued boiling, a specific gravity of 94° Tw., or a temperature of 270° Fahr., is attained, a little more nitre is introduced (if requisite), and the whole after an hour or two allowed to cool down. The clear liquor is run into a settler; the salts left behind are washed with a little water to free them from nitre, and then removed and drained to be employed for the manufacture of common "caustic ash." The thoroughly settled liquor is run into a caustic pot. It appears then of a dark straw colour, and on boiling gives off ammonia copiously. In this case all the nitre ought to be added in the pans, and only very little, if any, should be put into the pots during the finishing operation. The pot is fired carefully till a sample tests 60 per cent. alkali, which is the usual strength for cream caustic. It is not necessary to go further and bring the batch to igneous fusion, but it is baled out in that state, and without leaving any bottoms. Occasionally, however, the batch turns red, and in this case nothing is left but to pack it and sell it for inferior caustic, or else to fire it to igneous fusion and make it into white caustic. The oxidation by means of a current of air, instead of the nitre, is inadmissible for cream caustic, as the finishing temperature is too low. The cream colour is due to the presence of ferric oxide, which is held in suspension by the caustic soda at its comparatively low finishing temperature, and which separates on dissolving it in water. When cream caustic is prepared from uncausticized red liquor, as much as 1 cwt. of nitre per ton of it is required; but the cost of evaporation is much less, and the time is saved altogether.

In the manufacture of caustic soda, water is an item of considerable importance, as for every ton of 70 per cent. caustic, 14½ tons of water have to be evaporated. In well-conducted works 100 tons of "saltcake" (sulphate of soda) produce 54 to 57 tons of 60 per cent. caustic soda, of which 9 to 11 per cent. are "bottoms." The amount of salt necessary for reduction to 60 per cent. is generally 15 to 16 per cent. of the caustic soda packed; that of nitre 1½ to 2 per cent., of which about one-half is recovered in the form of caustic alkali. The total quantity of fuel used for all purposes should not exceed 6 to 6½ tons, divided as follows:—

	Tons.	Cwts.
Ball-furnaces, mixing,	1	0
" firing,	2	0
Boat pans,	2	0
Caustic pots,	1	0
Boilers,	0	10
Total,	6	10

The wages (including repairs) should be within 40*s.* per ton, and the following general calculation is given by Morison, to whom the above statements of yield and costs are due as well:—

		s.	d.	£	s.	d
Fuel,	6½ tons at	7	0	2	5	6
Saltcake,	37 cwts. at	3	3	6	0	3
Limestone,	22 "	0	4	0	7	4
Lime,	11 "	1	0	0	11	0
Salt,	3 "	0	8	0	2	0
Nitre,	40 lbs. at	0	1½	0	5	0
Wages,				2	0	0
Water,				0	1	6
Drums,				0	16	0
Charges and shipment,				0	15	0
Office expenses and management,				0	5	0
Interest on capital, depreciation, and stores,				0	16	0
Total cost f.o.b., Liverpool,				14	4	7

This was the cost of 60 per cent. *white* caustic in 1874; but evidently it must be made more cheaply in years of cheaper coal, &c., as it is often sold below the above price

Utilization of Tank Waste.—Only those attempts in this direction which have been crowned with some measure of success will be mentioned in the following:—

Hyposulphite of Soda (or Lime) from Tank Waste.—W. S. Losh in 1852 patented the following process:—The waste is exposed to the air for some time (a week will do). The mass is then lixiviated, and the solution contains partly sodium, partly calcium hyposulphite. By adding some sodium carbonate all hyposulphite is converted into the sodium salt which is separated from the precipitate of calcium carbonate, and the solution is concentrated by evaporation. The crystals of sodium hyposulphite are purified by redissolving. This process has ever since been carried out successfully at the Walker Alkali Works, near Newcastle-on-Tyne.

E. Kopp has modified the process by mixing the waste with 10 to 15 per cent. sulphur and 12 to 15 times its weight of water, and boiling it for an hour. The solution of calcium polysulphide thus obtained is put into a closed vessel furnished with agitating gear, and treated with sulphurous acid, drawn off and settled. The clear liquor is now a solution of calcium hyposulphite, which can be recovered by slow evaporation and crystallization. Stevenson has shown that this process can be carried out safely, without decomposing the salt, by using a vacuum boiler. If sodium hyposulphite is wanted, the calcium salt is decomposed by sodium sulphate, the solution separated from the gypsum, concentrated, and allowed to crystallize.

It must be borne in mind that the demand for hyposulphites is a very limited one, and that even the most successful process for their manufacture can only apply to a comparatively trifling portion of the tank waste produced in alkali works. The methods for recovering the sulphur from the *whole* of the waste are, therefore, of much greater importance.

Recovery of Sulphur from Tank Waste.—Three processes have been carried out in the large practice for this object, and a combination of the last two of them is now frequently employed. In order of time it seems as if Schaffner had found out his method first, followed by Mond shortly after, and quite independently; Hofmann's process was invented last of all, though described here first.

Process of P. W. Hofmann (1866). — The tank waste is oxidised in heaps, and it is mixed at the same time with ferric oxide obtained in its working up, as will be seen below; this greatly assists the oxidation. After six or seven days the waste is lixiviated, and yields a liquor containing mostly polysulphides. The residue is oxidised again, lixiviated, and the same process repeated a third time; the last liquor contains more hyposulphites. The lixiviation takes place in methodically arranged vats. The liquors are all united, and decomposed by means of the acid "still liquor" (from the manufacture of chlorine by native manganese). The free acid and chlorine, and the ferric chloride, are all active in decomposing the sulphide and hyposulphites; and if the proportions of the liquors were right, only sulphur is precipitated, but no sulphuretted hydrogen is evolved. As this is not always avoidable, the liquors are first mixed in a closed apparatus and the gas is conducted through a small wood fire, which inflames the sulphuretted hydrogen; the sulphurous acid is conducted into a tank containing "yellow liquors" from the lixiviation of waste, and this converts its polysulphides into hyposulphites. The separated sulphur is washed and dried; the neutral manganese chloride is treated with fresh tank waste and a little lime, till all iron is precipitated and the ferric oxide mixed with the bulk of the waste for oxidation, as mentioned above. The manganese chloride, now quite free from iron, is treated with "yellow liquor," which results in a precipitate of manganese sulphide containing free sulphur. After drying and calcination (during which the sulphur is turned into sulphurous acid, and the latter conveyed into a sulphuric acid chamber) a residue is obtained consisting of a mixture of Mn_3O_4 and $MnSO_4$; the latter is removed by lixiviation and the residue sold to glass works, for which it is valuable on account of its freedom from iron. The manganese sulphate is recovered in a pure state by evaporation; it is mixed with sodium nitrate and calcined in the sulphur furnace. The result is sodium sulphate and manganese nitrate; the latter, however, is at once decomposed into a mixture of different oxides of manganese and nitrogen tetroxide (N_2O_4), which gas enters the lead chambers and there acts in the well-known manner. The residue is lixiviated. The solution of sodium sulphate is used for manufacturing this salt, or for making "pearl hardening" (sulphate of lime); the residue corresponds to a manganese ore containing 55 per cent. of peroxide, and is used for manufacturing chlorine in the usual stills.

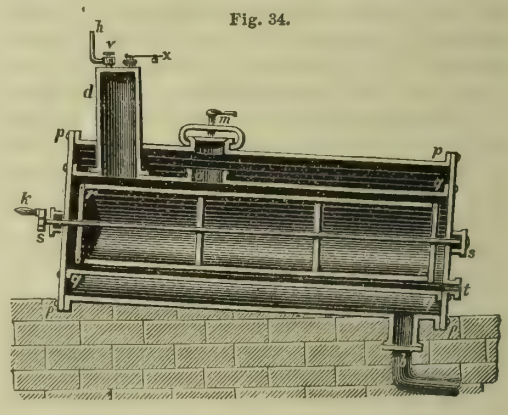
Hofmann's process has been used for a number of years in the large works at Dieuze, in Lorraine; but it has not spread any further, and it is not likely to do so, since Weldon's manganese recovery process is much simpler and more economical.

Besides, the very great complication and large number of operations, causing a corresponding amount of manual labour and skilled supervision, would seem to make the process not easily workable in this country. So far as the recovery of manganese is concerned, it has been superseded by Weldon's process even at Dieuze itself.

Schaffner's Process.—(Used since 1862 on a large scale, patented 1865).—The tank waste is allowed to weather in heaps for several weeks, till its colour has become greenish-yellow; the oxidation going on in the meantime is witnessed to by a considerable development of heat. The mass is broken up, and left again for twenty-four hours, and then lixiviated; the yellow liquor resulting contains polysulphides and hyposulphites. The residue is again oxidised, but this time in the tanks themselves in which it has been lixiviated, and which are connected and fitted up like the ordinary (Shanks') soda tanks. This is done by blowing the warm gas from a neighbouring chimney underneath the false bottoms of the tanks, and thus through the mass, by means of a fan blast. Six to eight hours suffice for this; the mass is then lixiviated, oxidised again, and lixiviated a third time. The mixture of liquors ought to contain a suitable proportion between polysulphide and hyposulphide, similar to what Mond prescribes (see below). The special peculiarity of Schaffner's process, and that which seems to be its greatest recommendation, is the ingenious way in which he treats the mixture of yellow liquors. It is based upon the following facts:—In a liquor containing at the same time hyposulphites and polysulphides, hydrochloric acid, in the first instance, decomposes the polysulphides, and that with precipitation of sulphur and evolution of sulphuretted hydrogen. The hyposulphites in such liquor are decomposed later on by hydrochloric acid, yielding gaseous sulphurous acid, and also precipitated sulphur. The polysulphides in such liquors, if sulphurous acid is passed through them, are converted into hyposulphites, again with precipitation of sulphur.

These reactions are practically carried out in a pair of vessels made of stone or (preferably) of cast iron, furnished with steam pipes, trial cocks, gas-delivery pipes, &c., which work in this way, that in each of them, turn by turn, sulphurous acid is evolved and conveyed into the other one. Only once—*i.e.*, in the very beginning of the work—is sulphuretted hydrogen evolved. When both vessels have been filled with yellow liquor, hydrochloric acid is run into one of them up to the point at which all polysulphides are decomposed. These are converted into chlorides, sulphur is precipitated, and sulphuretted hydrogen is given off, which escapes through the second vessel into the open air, for this one time. Now everything is ready for constant work. Henceforth the acid only acts upon hyposulphites; it only evolves sulphurous acid, which is always used for converting the polysulphides of the next following portion of liquor into hyposulphite, always with precipitation of sulphur. This happens at once by running more hydrochloric acid into the first vessel. When no more sulphurous acid is evolved from it, steam is blown into the liquid to drive off that which is absorbed in it, and the whole, liquid and sulphur, are let out by opening a screw valve at the bottom. The vessel is recharged with yellow liquor, and now hydrochloric acid is run into the second vessel, whose contents are now all converted into hyposulphite, so that only sulphurous acid is evolved, which is carried back into the first vessel, and thus the play of the apparatus continues constantly, turn by turn for each vessel. The decomposed liquid contains essentially calcium chloride, a little sodium chloride, calcium sulphate (partly from the oxidation, partly from the sulphuric acid contained in the hydrochloric acid employed, partly from secondary decompositions), along with the precipitated sulphur. The mixture is run on to filters, and the sulphur washed out to a certain extent. The way in which it is further purified and converted into a saleable state is another important feature of Schaffner's process. He mixes the sulphur with sufficient water to form a thin paste and some milk of lime, and runs it into a peculiarly-constructed melting apparatus, whose construction will be made clear by the subjoined woodcut (Fig. 34). Two cylinders are firmly joined together—an outer one of wrought iron, *p p*, and

Fig. 34.



an inner one of cast iron, *q q*. The ends are common to both, and a mechanical stirring apparatus, *r*, passes through them, through stuffing boxes, *s s*. The whole is mounted in an inclined position. The paste of sulphur, water, and a little lime (along with impurities) is charged through the man-hole, *m*, and the corresponding opening, *o*, in the inner cylinder, into the latter. When the man-hole has been closed again, steam of $1\frac{3}{4}$ atmospheres' pressure is blown in through the pipe, *b*. It first circulates round the inner cylinder, then enters the latter through *o*, is brought into intimate contact with the mass in the same by means of the stirrer, and ultimately finds its way into the dome, *d*, which is provided with a valve, *v*, an exit pipe, *h*, and a safety valve, *x*. The sulphur is melted by the heat of the steam, and when the stirrer is stopped, it gathers in the lowest part of the inner cylinder; whilst the specifically higher liquor, containing the calcium sulphate mechanically

suspended, floats on the top. The sulphur is run off through the opening, *t*, and cast into moulds, whilst the liquor runs to waste. The object of the addition of lime is both to saturate any excess of acid and to form a little calcium sulphide, which combines with any arsenic (from the raw materials) to calcium sulpharseniate, soluble in water, and therefore removed along with the supernatant liquor. It will be observed that the contents of the inner vessel cannot be forced back into the steam pipe, as would happen if the latter entered direct into the mass; and, on the other hand, the agitation by the stirrer causes a much more direct heating and action on the sulphur than a mere jacketing with steam could produce.

Schaffner's method is practised in many works on the Continent with perfect success, more particularly since he has adopted (from Mond's process) the oxidation in the tanks themselves for the second and third time; but it must be stated that his mode of decomposing the yellow liquors, ingenious as it is, has been objected to as yielding too little sulphur and too much calcium sulphate. This will be spoken of further on.

Mond's Process.—(Discovered about 1860, patented 1863). The first experiments were suggested by Guckelberger, who, however, did not pursue it to a practical issue, so that Mond must be fully credited with the merit of having made the process a success. Mond tried from the first to hasten the oxidation of the waste by an artificial current of air, and this is the special feature of his process. At first he exposed it to the current of air on shelves; but this had to be abandoned on account of the large amount of time, and space, and labour required. He then found that the waste obtained by the method of lixiviation (Shanks') now universal in this country can be oxidised in a much simpler manner, viz., by blowing air direct under the false bottom of the lixiviating tanks. The number of the latter must be trebled, and each of them is, apart from its other fittings, provided with a 3-inch branch from an 8-inch air main, in which a Schiele's 30-inch fan blast maintains a constant pressure of 3 or 4 inches (water). As soon as the last soda liquor has been run off any of the tanks, the blast is put on by taking out a small damper in the air-pipe branch. This is, however, not done by haphazard; even the indication of the ordinary air-gauge in the main is not sufficient, as with equal pressure in the main the effect on the waste might vary very much according to its density, and consequently its permeability for air. Mond tries, therefore, by means of a differential ether anemometer, what real quantity of air passes through the waste, and this is done for every tank. The operator very soon knows for each size of tank how many degrees of the anemometer are required to oxidise the waste, so that on subsequent lixiviation it may yield a liquid of the proper composition. It is found in practice that the false bottom is quite sufficient to cause an equal distribution of the air through the waste, even if (as necessary for conveniently cleaning out the tanks) the air-pipe is fixed in one of the corners. The waste soon begins to heat, rising up to 200° Fahr.; it gives off quantities of steam, and becomes gradually covered by spots of a bright yellow colour, which, together with the temperature and the quantity of steam passing off, enable the workman to judge very well when he is to stop blowing. Usually twelve to sixteen hours are required for this. During the blowing mostly no sulphuretted hydrogen whatever is given off; but occasionally this is the case to a very slight extent. The oxidised waste is then lixiviated, first with weak liquor from a previous operation, of about 6° to 8° Tw.; what runs off is strong liquor of 18° Tw., and is run as such to the decomposing tubs till it has gone down to 10° Tw. Water is now run on the top, and what runs off at the bottom is collected in a cistern as weak liquor, to be used in the next operation; this is continued till the strength of the running-off liquor is only 2° or 3° Tw. The water is now stopped, and the first lixiviation thus at an end; it takes from eight to nine hours. Now the air-blast is put on for the *second* time, followed by a second lixiviation, a *third* blowing, and a third lixiviation. Where there is not sufficient room the waste is only blown twice, but this is not advisable. It is, indeed, best to blow it four or even five times, in order to make the ultimate residue more harmless; but this is only practicable where the operation is not carried out in the soda tanks, but in tanks specially constructed for the purpose. After the waste has been cast out of the tanks, they must be cleaned and washed out most carefully, in order to remove every particle of sulphur liquor, which would of course be most injurious in the next lixiviation of black-ash balls, now immediately following. For the same purpose it is advisable to put a false bottom in the tank, made of bricks and cement, sloping towards the run-off cock, so that no liquor can lodge anywhere underneath the perforated bottom. It cannot be denied that the work with Mond's tanks, in combination with the ordinary ball lixiviation, is somewhat complicated; that by the least carelessness of the workmen the soda liquors are liable to become contaminated with more or less sulphur liquor; and that the whole arrangement of trebling the tanks and providing them with a large number of additional fittings is very cumbersome. It would therefore seem advisable not to interfere with the ordinary soda tanks at all, but to cast the waste from them in the usual manner, and subject it to the blowing, &c., in a separate set of tanks altogether; and in some factories this is now usually done.

Mond's great merit is to have drawn special attention to the necessity of directing the oxidation methodically, so as to obtain liquors of a special composition; of having devised the means for doing so; and of having prescribed easy and expeditious plans for testing the liquors for the same object. It is very well known that in the course of the oxidation, be it the slow one by spontaneous action of the air, or the quick one by Mond's blast, which acts in as many hours as the other takes days or weeks, in the first instance principally polysulphides

and hydrosulphides are formed, which are afterwards more or less oxidised to hyposulphites. Later on the hyposulphite is decomposed into sulphur and sulphite, both of which are insoluble and lost in lixiviating; and this is, of course, equally the case with the ultimate product, calcium sulphate, which, however, is always found in the mass. It is therefore evident that the oxidation must not be carried on any further than necessary, and this is done when the proportion of sulphides to that of hyposulphite is as nearly as possible 2 : 1. In this case the reaction with hydrochloric acid runs as follows:—

$$2CaS + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 4S.$$

The hydrosulphide, CaH_2S_2, and the bisulphide, CaS_2, or any other polysulphides, behave just like CaS, which, indeed, cannot exist as such in the liquor, being insoluble; but the reaction is shown for it for the sake of simplicity. If in any liquor the sulphides prevail over the above proportion, there will be an evolution of H_2S; or if the hyposulphites prevail, of SO_2, both of them causing a nuisance as well as a loss of sulphur. In practice it is not possible to attain the above proportion exactly, and as more harm is caused by an excess of sulphides than by their deficiency, the proportion is kept slightly the latter way. It has been stated above that the anemometer serves for regulating the oxidation according to the tests of the liquors. The analysis of the latter is performed by Mond as follows:—1. The hyposulphite is estimated as usual by a decinormal solution of iodine and starch, after having first separated the sulphides by zinc chloride and filtering. 2. To a certain quantity, say 3·2 c.c. of the liquor, a little starch solution is added, and then a standard solution of iodine, till it turns blue; the quantity is noted; the liquor is then again decolorized by a drop of sodium hyposulphite solution, litmus is added, and a standard solution of soda is turned in till the liquor is neutral. The following reactions take place simultaneously:—

$$\begin{cases} 2(CaS_2O_3) + 2I = CaI_2 + CaS_4O_6. \\ CaS_2 + 2I = CaI_2 + 2S. \\ CaH_2S_2 + 4I = CaI_2 + S_2 + 2HI. \end{cases}$$

And subsequently the free HI is disposed of thus:

$$2HI + Na_2O = 2NaI + H_2O$$

The standard soda thus shows directly the hydroiodic acid, and indirectly the equivalents of hydrosulphide; the iodine used in the *first* titration is that of hyposulphite, and that used in the *second titration*, deducting the two former numbers, that of sulphide (polysulphide). Using for both titrations 3·2 c.c. of liquor, and decinormal solutions, and presuming that the polysulphide is bisulphide only (this is, however, refuted by Stahlschmid's researches, who finds it to be mostly tetra- and penta-sulphide), we have simply to add together the measures of iodine used in both titrations, subtract that of caustic soda, and divide the remainder by ten, in order to find the total percentage of sulphur in the liquor; and from this the hydrochloric acid can be easily calculated, as each 32 of sulphur require 36·5 of HCl.

When it is only required to see whether the proportion is a favourable one for decomposition, it need only be noticed whether the measure of iodine used *after* precipitating the sulphides by zinc solution to that used for the original liquor is nearly 1 : 5, and it ought to be rather below than above 5; that is, there ought to be rather *less* than *more* than 2 equivalents of sulphide for one of hyposulphite. Mond believes that the decomposition of calcium hyposulphite is not as simple as usually explained, viz.—

$$CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + H_2O + S;$$

but that a great deal of it is decomposed with the formation of calcium trithionate, thus:

$$5CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 2CaS_3O_6 + 4S.$$

On boiling the calcium trithionate is decomposed into calcium sulphate, sulphur, and sulphurous acid; the latter re-forming trithionate and so forth, till nothing but sulphur and calcium sulphate remain besides calcium chloride and water. Stahlschmid's researches bear out Mond's statements in this case. This means a loss of acids and sulphur, as calcium sulphate is worthless, and for this reason Mond rejects Schaffner's method of decomposing the yellow liquors, and rather runs the latter into a large wooden tub at the same time with common weak muriatic acid from the post-condensers (wash-towers), just sufficient to decompose them; if the proportion of sulphides be rather less than two to one hyposulphite, if the temperature be kept at 140° to 150° C., and if the liquor is thoroughly agitated by a mechanical stirrer, no gas whatever is evolved, the liquor keeping the slight excess of SO_2 in solution, and the sulphur is precipitated free from ferrous sulphide. By taking a sample from time to time, and observing whether it is of the proper colour, the workman can judge whether there is not too little acid, and he tries whether there is not too much either, by pouring a little yellow liquor into the samples, which ought very soon to produce a grey colour through formation of FeS; when too much yellow liquor is used before this grey colour appears, the flow of acid must be checked. The tub is covered in and connected with the chimney, to convey away any occasional escape of gas. It cannot be denied that it is not quite easy, in ordinary work, to work altogether without evolution of sulphuretted hydrogen, especially in commencing the process, since workmen cannot always be trusted to be sufficiently careful; and as Schaffner's apparatus does not allow any such escape under any circumstances, it would appear as if its use were advisable, even if, as Mond asserts and as Stahlschmid has confirmed, rather less sulphur is yielded by it than by the decomposition on his principle—at least in such cases where any escaping gas would cause complaints in the immediate neighbourhood. Schaffner has, however, always maintained that no trithionate and consequently no calcium sulphate is formed, if the operation is carried out exactly as prescribed by him, and Lunge's researches have proved this to be the

case. The calcium sulphate found in SCHAFFNER'S sulphur only proceeds from the sulphuric acid always present in common muriatic acid.

There is nothing peculiar in MOND'S way of filtering, washing, and drying the sulphur. He used to melt it by an apparatus different from SCHAFFNER'S, probably only for the reason that the latter was protected by patent; but it does not appear that any of the many modifications proposed is equal to SCHAFFNER'S melting process.

MOND'S process has been carried out for many years past by several English alkali works, and must be pronounced successful, especially if combined with SCHAFFNER'S melting apparatus, and if carried out in separate tanks, so that four or five repetitions of the oxidation can be practised.

By none of the methods hitherto proposed is the tank waste really "desulphurised." In the *best* case, about half of the sulphur combined is recovered as such, mostly less than that; one factory in Lancashire obtains 6 per cent., another, near Bristol, 8 per cent. of sulphur upon the sulphate of soda originally balled. The remainder, to some like extent, is lost in a gaseous form during the recovery process; mostly, however, it exists in the oxidised and lixiviated waste as calcium sulphite and sulphate, even of free sulphur, and *always* to a certain extent of calcium sulphide, even after many successive oxidations. This "desulphurised" waste is of course very much less liable to give rise to a nuisance than ordinary tank waste; but it would seem desirable to dispose of it otherwise than by depositing it on waste ground, and perhaps MOND'S proposal to burn it in cement kilns, and use it similarly to SCOTT'S selenitic mortar may lead to its better utilization. MACTEAR has patented a plan for dealing with the yellow liquors from old tank heaps. Its only new feature is the treatment of such liquors by sulphurous acid, in order to "correct" them, and to make their composition similar to that indicated above; after this the ordinary process of MOND is carried out.

Cost of Production.—The following calculation shows the actual cost of production (from the manufacturing books) of soda ash (yellow carbonate), at a Tyneside manufactory in the beginning of 1876.

	Tons.	£	s.	d.	£	s.	d.
Spanish cupreous pyrites, 48 per cent. (copper not paid for),	0·8626 at	0	16	0	0	13	9
Nitrate of soda (deducting from the price the value of the nitre cake),	0·0155 at	10	10	0	0	3	3
Common salt,	1·3175 at	0	18	0	1	3	9
Chalk,	1·732 at	0	4	0	0	6	11
Coals for mixing,	0·750 at	0	6	0	0	4	6
" for firing,	2·410 at	0	5	0	0	12	1
Wages,					1	14	9
Repairs and stores,					0	11	1
Removal of tank waste,					0	2	6
Casks and delivery on board ship,					0	12	0
Management, foremen, general expenses of all kinds,					0	9	4
					6	13	11

This is the cost of a ton of ash, f.o.b. in the Tyne, such as it is furnaced, whether 51 or 53 per cent., as made by the old hand-furnace; revolver ash is cheaper and stronger. It is scarcely necessary to say that several or even most of the items differ according to the variations in the price of raw materials (pyrites, for instance, was fully 25 per cent. cheaper in 1876 than in 1875), in the size of the factory, its local advantages or drawbacks, and the skill and care displayed in its management.

JAMES YOUNG, F.R.S., revived in 1871 the ammonia process for making carbonate of soda, which had been patented, if not originally invented, by DYER and HEMMING. The reaction worked out by these chemists nevertheless failed to produce in their hands a good commercial process, on account of the loss of ammonia in the manufacture. YOUNG'S improvements consist in a method of working by which the ammonia, when once put into the apparatus, is never again exposed to the atmosphere. The vessels communicate with each other, so that when carbonate of ammonia is mixed with the common salt, treated with carbonic acid, and decomposed, forming bicarbonate of soda and chloride of ammonium, this latter salt is passed through a close tube into another vessel, where it is decomposed by lime, and the ammonia passed along with carbonic acid into a second solution of common salt, and so on continuously, making a circuit of the vessels. Part of this carbonic acid is obtained from the solution of bicarbonate of soda, which is boiled in the vessel in which it is formed, until it gives off part of its carbonic acid and any ammonia which may remain attached to it.

This process was carefully worked at by YOUNG for a long time, and its practicability fully demonstrated, before he made it known; but he never brought the soda into commerce, not wishing again to enter into business, but preferring to leave the matter to others. There is a probability that it will come more extensively into use, as the work is easy, and it is free from the so-called noxious vapour—muriatic acid. The value will greatly depend on the price of ammonia; but it will also depend on the convenience of the position, as the ammonia process may be carried on where the acid process could not be permitted. At any rate, this is an important new process of manufacture, and its true value will not be easily seen for a long time. Should circumstances at any time render ammonia even but a little cheaper, it would probably become a very general process.

SODIUM.—*Sodium*, English and French; *Natrium*, German and Latin. Symbol, Na; atomic weight 23.—This metal was isolated in 1807 by SIR HUMPHREY DAVY, through the agency of voltaic electricity. Moistened sodium hydrate was employed, the oxygen both of the water and of the soda was liberated at the positive pole, and the sodium and hydrogen at the negative pole.

Sodium is a monatomic metal. With chlorine, fluorine, bromine, and iodine, it forms the compounds NaCl, NaFl, NaBr, NaI; with oxygen it forms a monoxide (Na_2O) and a dioxide (Na_2O_2); with sulphur a monosulphide (Na_2S), and its hydrate (NaHS), and many polysulphides.

The processes already described for the produc-

tion of potassium are applicable also, with slight modifications, for the preparation of sodium. The apparatus required is also of exactly the same description as in the case of potassium. The substances employed may be either sodium hydrate and iron, or sodium carbonate and charcoal. These are placed in a malleable iron bottle—those in which mercury is imported answer admirably—and heated to whiteness in a powerful blast furnace. The gas, which is evolved at the beginning of the process, is of a yellow colour; this is allowed to escape into the air, the receiver not being adapted to the retort till a cold iron rod thrust into the bottle comes out covered with globules of sodium, which take fire in the air. The sodium vapour is then conducted into a receiver (which may be of iron or copper) containing mineral naphtha or rock oil; it is kept cold by surrounding it with cold water, which is frequently changed. It should, of course, be provided with a vent for the escape of the incondensable gases evolved during the decomposition. The operation is much more productive than in the case of potassium, because the sodium does not combine with carbonic oxide.

The decomposition either of sodium hydrate by metallic iron, or of carbonate of soda by charcoal, is, however, effected with greater difficulty than is the case with the corresponding potassium salts. By mixing the sodium hydrate or carbonate of soda with a little potassium hydrate or carbonate of potassium, the operation is effected with greater facility; but the metal obtained is then a brittle alloy of sodium and potassium. From this, however, the whole of the potassium may readily be separated by means of slow oxidation, without any considerable loss of sodium. To effect this, the alloy is formed into plates and placed in a large bottle; these are covered with naphtha, and the air in the bottle is occasionally removed. After a few days the whole of the potassium will have disappeared, and pure and very ductile sodium remains. In SCHOEDLER's process the carbonate of soda used is obtained by the ignition of sodium acetate, free access of air being avoided. The object of this is to obtain the carbonate in a very pure state, since, if sodium sulphate be present, it becomes reduced in the process to sodium sulphide, which acts strongly on the iron bottle. The mixture of carbonate of soda and charcoal obtained is mixed with a fourth of its weight of charcoal in fine powder, and with double this quantity of charcoal in a coarse state, to prevent fusion of the mass. Should this occur, the fused contents spirt into the tube and choke it up. The mixture, heated in the iron bottle, yields pure sodium, with a very small residue of carbon, &c.

The process now commonly employed for the preparation of sodium was devised by H. St. C. DEVILLE. Crystals of sodium carbonate are calcined, powdered, and mixed with a slight excess of powdered charcoal or coal: chalk is also added to keep the mixture fluxed during the process. In preparation in small quantity the proportions are:—

Dry carbonate of soda,	717 parts.
Charcoal,	175 "
Chalk,	108 "

When the continuous process is used, which will be described further on, the proportions are:—

Dry carbonate of soda,	30 parts.
Charcoal,	13 "
Chalk,	3 "

The materials are pounded and sifted, then mixed by hand and again sifted, in order to insure their intimate association. The mixture must be used as soon as made, lest moisture be absorbed. It is also considered advantageous, when circumstances permit, to calcine the whole mass before introducing it into the distilling apparatus; since it is thereby rendered much more compact, and a larger quantity can be operated on in a vessel of a given size.

The distillation is performed either in a mercury bottle or in iron cylinders of large dimensions. The receiver preferred by DEVILLE is that designed by MARESCA and DONNY for the condensation of potassium. These receivers are made of two plates of iron from one-twelfth to one-eighth of an inch thick: one of them, A, Fig. 1, is turned up at the edges, while the other, B, is left flat, except at the end, C, where both plates are formed into a cylindrical neck, 1 inch in internal diameter. The conical portion, which joins the cylindrical neck to the flat body of the receiver, should be made as short as possible.

Fig. 2.

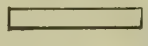


Fig. 1.

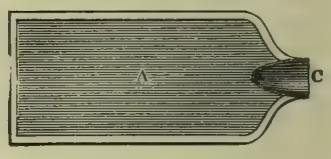
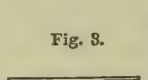


Fig. 3.





The two portions when joined form a rectangular box with a cylindrical neck. These receivers are either left completely open at the back (Fig. 2), or they are closed at the back, with the exception of a small aperture near the top, Fig. 3. The plates are held together by iron clamps.

With the first apparatus (Fig. 2) the condensed sodium (so soon as the receiver becomes hot enough to retain it in the liquid state) flows off as fast as produced; with the second (Fig. 3) the sodium fills the receiver, which is then removed.

When the process goes on well the sodium is very pure. Some impure sodium remains attached to the plates of the receiver; hence the plates should always be scraped before again using them, the matter scraped off being received under rock oil, and redistilled.

The temperature absolutely required for the reduction of sodium carbonate is about that required

for zinc smelting; but a larger product is obtained when it is raised to the melting point of magnetic oxide of iron.

For large operations iron cylinders are used, which are so arranged that they can be discharged and fed without removing them from the furnace, or extinguishing the fire. The cylinders, made of wrought iron (T, Fig. 4), are about 4 feet long, $5\frac{1}{2}$ inches internal diameter, and half an inch thick. They are open at one end, O, and closed at the other end, P, except that this extremity is pierced with a circular

Fig. 4.

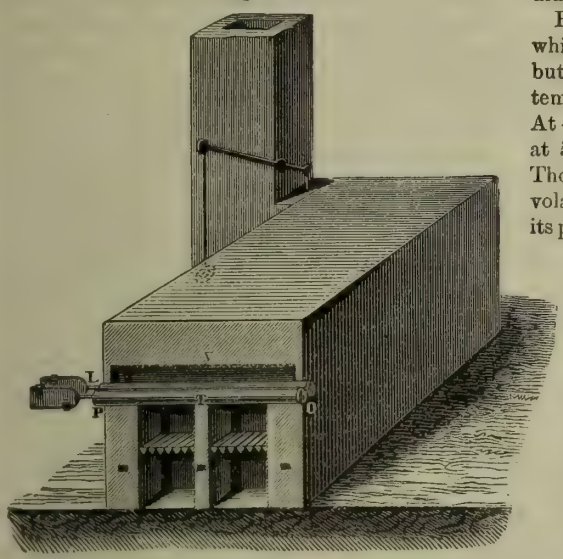
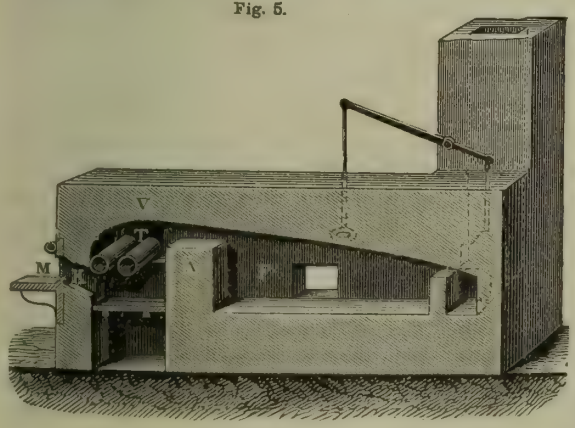


Fig. 5.



aperture, to which an iron tube, L, is adapted, having a conical termination for connection with a receiver of the form already described. The open end, O, is fitted with a wrought-iron cap terminating in a hook. The iron cylinders must be protected from the action of the fire by coating them with fire-clay, and inclosing them in tubes of refractory earthenware.

The cylinders are heated in a reverberatory furnace, Figs. 4 and 5, the fire-place of which is divided into two equal parts by a wall of fire-brick 18 inches high, on which the middle of the cylinder rests. The fuel is introduced through K, and heaped on a shelf, M, so as to close the aperture while the process is going on. A wall, A, reaching a little above the cylinder, keeps the flame vertical, and the low arch, V, causes it to circulate round the cylinders.

The soda mixture is introduced in paper or canvas bags, and the tube is closed by the cap and luted with fireclay. When the process is finished a little water is thrown on the cap; this cracks it off, and the residue of the charge, which is a spongy mass of lime and charcoal mixed with caustic soda, &c., is withdrawn and washed with water to extract the alkali.

PROPERTIES.—The colour of sodium is a silver white; its lustre is more brilliant than that of lead, but scarcely equals that of silver. At the ordinary temperature it is solid, but soft and ductile like wax. At —20° C. it is rather hard, at 0° C. very ductile. at 50° C. it is semi-fluid, and at 97·6° perfectly so. Though less fusible than potassium, it is more readily volatile, and hence a less intense heat is required in its preparation. It crystallizes on cooling in octahedra.

When exposed to the air it quickly becomes tarnished, owing to the formation of a crust of soda; and if heated nearly to redness it inflames, and emits brilliant scintillations. The specific gravity of sodium is 0·97 at 50° C., and it is consequently lighter than water; and if thrown into this liquid exposed to the air it swims about, presenting the appearance of a silvery-fused globule, constantly decreasing in size and producing a hissing noise, owing to the escape of hydrogen gas. These phenomena continue until the whole is dissolved as soda.

Potassium under the same circumstances takes fire, and continues to burn until dissolved; but sodium, in decomposing water, either produces less heat or requires a higher temperature to inflame it. If, however, the water be thickened with gum, so as to retard the movement of the sodium over the surface, or if there be only a few drops of water, the metal then ignites.

Sodium dissolves in ammonia gas under pressure, forming a blue solution which, if evaporated slowly, yields crystals of the metal (SEELEY, *Chem. News*, xxiii. 169).

The alloys of sodium are prepared by fusing it with the respective metals. Potassium and sodium alloy is fluid at ordinary temperatures. It can be prepared by melting the metals together in a tube containing caoutchin (GREVILLE WILLIAMS); or by heating acetate of potassium with sodium (WANKLYN).

Sodium, like potassium, decomposes most oxides, metallic and non-metallic; also by far the greater number of salts, deoxidising not only the acid but the base also, if it happen to be the oxide of a heavy metal. When thrown upon the surface of mercury, sodium forms an amalgam, with the production of heat and light; this does not take place with potassium. Sodium is employed in the arts, principally in the preparation of aluminium, by the decomposition of the chloride of that metal.

STEEL.—*Acier*, French; *Stahl*, German. Few manufactures have undergone more important changes, and made more rapid strides within the last twenty years, than that of steel. Indeed the changes, not only in the modes of manufacture, but also in the properties of the metal, have been so great that it has become extremely difficult to define what is the meaning of the term steel. The chief characteristic of the metal termed steel twenty years ago was its property of becoming hardened by heating and plunging into cold water, and its almost sole use was for making edge tools. Modern modes of manufacture have so enormously increased the quantity and decreased the price, while at the same time they have introduced so many new varieties of the metal, that it is now used far more extensively for other purposes, such as railway bars, castings, and plates, than it is for the older manufacture of cutting tools. This has led to the extension of the use of the term steel to varieties which no longer accord with the old definition, and it becomes necessary to try to find a new one. This is exceedingly difficult, because the usage of practical men has sanctioned the application of the term to alloys which have many of the properties of wrought iron, and are entirely devoid of one quality that used to be considered the generic characteristic of steel. Scientific writers have endeavoured to draw a distinction between iron and steel based upon inherent properties, while practical manufacturers and users have by common consent come to apply the terms according to the mode of manufacture. With the object of settling the nomenclature of iron and steel an International Committee was appointed at Philadelphia by the American Institute of Mining Engineers. The Committee consisted of Mr. I. Lowthian Bell, M.P., Dr. Hermann Wedding, Professor Tunner, Professor Akermann, M. Grüner, Mr. A. L. Holley, and Mr. T. Egleston; and they resolved upon the following recommendations:—

I.—That all malleable compounds of iron, with its ordinary ingredients, which are aggregated from pasty masses, or from piles, or from any form of iron not in a fluid state, and which will not sensibly harden and temper, and which generally resemble what is called wrought iron, shall be called *weld-iron*.

II.—That such compounds, when they will from any cause harden and temper, and which resemble what is now called "puddled steel," shall be called *weld-steel*.

III.—That all compounds of iron, with its ordinary ingredients, which have been cast from a fluid state into malleable masses, and which will not sensibly harden by being quenched with water while at a red heat, shall be called *ingot-iron*.

IV.—That all such compounds, when they shall from any cause so harden, shall be called *ingot-steel*.

Siemens, when speaking upon this point in his Presidential Address to the Iron and Steel Institute (1877), remarks: "The nomenclature here proposed is entitled to careful consideration from the eminence, for both theoretical and practical knowledge, of the gentlemen composing the committee; but I apprehend that, for common use, the distinctions desired to be drawn are too manifold. Moreover, the lines of demarcation laid down run through materials very similar, if not identical in their application, where a distinction in name would be extremely difficult to maintain and awkward to draw. Take, for instance, railway bars from ingot-metal, which are usually specified to bear a given dead load without deflecting beyond certain limits, and to resist a certain impact without rupture. The materials answering to these requirements contain from ·2 to ·6 per cent. of carbon, depending in a great measure upon the mode of production, and upon the amount of admixture of phosphorus, sulphur, silicon, and manganese. But inasmuch as the quality of tempering is chiefly due to carbon, part of the rails delivered under such specification might have to be classified as ingot-iron, and part as ingot-steel. The Committee omits to define the degree of hardening which it considers necessary to bring a material within the denomination of ingot-steel; it is well known, however, that the temper depends upon the exact temperature to which the metal is heated before being plunged into the refrigerating medium, and also upon the temperature and conductivity of the latter, and that ingot-metal with only ·2 per cent. of carbon, when plunged hot into cold water, takes a certain amount of temper. The question of the amount of import duties payable in foreign countries upon metal occupying a position near the proposed boundary line would also lead to considerable inconvenience.

"Difficulties such as these have hitherto prevented the adoption of any of the proposed nomenclatures, and have decided engineers and manufacturers, in the meantime, to include under the general denominations of cast steel all compounds consisting chiefly of iron, which have been produced through fusion, and are malleable.

"Such a general definition does not exclude from the denomination of steel materials that may not have been produced by fusion, and which may be capable of tempering, such as shear steel, blister steel, and puddled steel, nor does it interfere with distinctions between cast steels produced by different methods, such as pot steel, Bessemer steel, or steel by fusion on the open hearth."

Although the common use of the term steel may render it impossible to find a definition that shall be logically correct, the difficulty of forcing into general use even so slight a modification of commonly accepted terms as the classification proposed by the Centennial Commission is so great, that it is probably better to define the body by its mode of manufacture than to attempt to introduce new terms for some products that are now commonly called steel, in order that others may be classified under this head in a logical manner, based upon a consensus of properties. If this were done, there could be little difficulty in agreeing that the term "steel" should be retained, as suggested by Whitworth and Siemens, for alloys of iron produced by fusion having great strength, and always using

as a prefix a term indicating the mode of manufacture. There could thus be no difficulty in understanding what is meant by pneumatic or Bessemer steel, open-hearth or Siemens steel, crucible steel, blister steel, puddled steel. If it is necessary to distinguish the different qualities of each kind, the classification might very well be dependent upon the tensile strength of the material. Thus, steel which will bear a tensile strain of 25 to 30 tons per square inch might be called, as indeed it now is in common usage, "soft"; from 30 to 35 tons might be called "mild"; 35 to 40 tons, "hard;" 40 to 50 tons, "extra hard"; leaving anything above this to be designated specially. This will very nearly accord with the classification proposed by Adolph Greiner, of Seraing, with the usage of Holley, and the recommendation of Hackney. The classification arrived at by the International Commission at Philadelphia last year was a very good one; but unfortunately makers and users will not adopt it, and therefore it becomes almost a dead letter. Our own Admiralty, the Board of Trade, and Lloyd's, for instance, still persist in calling what the Commission would have designated as "ingot-iron," either "Soft Bessemer or Siemens steel." There is no difficulty in understanding what they mean by these terms, while there might be some difficulty, as Siemens points out, in deciding whether a given plate would or would not harden, and therefore whether it was "ingot-iron" or "ingot-steel."

In this article the term steel will be used in its common and wider acceptation, and the various kinds will be considered in their chronological order.

There is great probability that an alloy of iron that would harden by sudden cooling, and that could be forged into edge tools, was discovered soon after the isolation of the metal itself was effected. At all events, Homer speaks of the art of tempering in such a way as to leave no doubt that in his time such an alloy was known. We have no record of the mode of production employed by the ancients, but it is feasible to suppose that it was by some modification of the plan still adopted by the Hindoos —viz., by melting wrought iron in crucibles in contact with carbon. Dr. Percy considers that this process of steel making is the most ancient, and he quotes from Dr. Buchanan's description of the process as he saw it practised in 1807 as follows:—

"A wedge of iron, forming about a third part of one of the little lumps produced in an ordinary Hindoo iron furnace, is put into a conical, unbaked clay crucible, of about the capacity of a pint, with the addition of 3 rupees' weight (531 grains) of the stem of *Cassia auriculata*, and two large green leaves of a species of *Convolvulus* or *Ipomœa*. The crucible thus charged is closed at the mouth with a cap of unbaked clay well luted on, and then well dried near a fire. The furnace used is a little circular pit in the ground, somewhat dilated at the top. An earthen pipe, connected with two bellows, each consisting of a bullock's hide, and which are worked alternately, enters the fire-place at the bottom. A row of crucibles is first laid round the sloping mouth of the fireplace; then within these another row is placed; and the centre of the arch thus formed is occupied by a single crucible, making in all fifteen. The crucible in the outer row, opposite the nozzle of the bellows, is then taken out, and in its stead an empty crucible is placed horizontally, with its mouth directed inwards. This crucible can be readily drawn out and replaced, and the opening which it closes constitutes the fire-hole through which fuel is introduced. The fuel is charcoal, with which the fireplace is filled, and the arch of crucibles, charged as stated above, is covered over. The bellows are then plied during four hours, when the operation is completed. A new arch of crucibles is constructed, and the process goes on night and day; five sets, of four crucibles each, being every day worked off. On breaking open the crucibles the steel is found melted into the well-known conical cakes of wootz, which usually present a radiated wrinkling on their upper or flat surface, considered by Buchanan to indicate a tendency to crystallization. The cakes are surrounded by some vitrified matter.

Henry found a sample of wootz to contain—

Carbon, combined,	1·333
" uncombined,	·312
Silicon,	·045
Sulphur,	·181
Arsenic,	·037
Iron, by difference,	98·092
	100 000

The following is an analysis of a sample of steel made from Indian ore reduced by Blair's process:—

Carbon, combined,	·400
" graphite,	—
Silicon,	·090
Sulphur,	·081
Phosphorus,	·028
Manganese,	1·200
Iron,	98·500
	100·299

It was very soft, but capable of taking an edge when hardened.

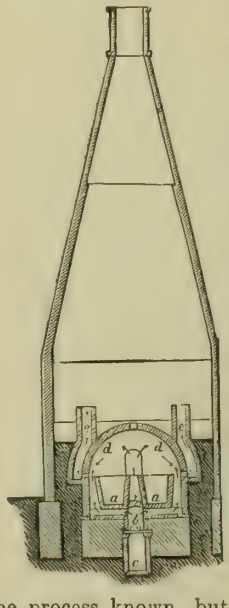
In the sixteenth century a very curious method was employed for making steel. This was described by several writers, among others by Vanoccio Biringuccio in 1540, and by Agricola in his "De Re Metallica," in 1560. This consisted in heating malleable iron in molten cast iron until the former became pasty, by which time it had absorbed sufficient carbon from the cast iron to convert it into steel. It was, in fact, a cementation process conducted at a very high temperature and with a fluid bath. The translation of the original, as given in Dr. Percy's work, is very curious, and well worth perusal.

Since steel occupies a medium position between cast and wrought iron, it is natural to expect that in the early stages of the manufacture of iron in finery hearths, it would often happen that the workmen would obtain a product more carburized than usual, and having, therefore, a steely nature. This was the case; and the Styrian, Carinthian, Tyrolese, Paal, and Siegen processes, which were largely practised

in the sixteenth century, are all modifications of a process of making *steel in finery hearths.*

The *Carinthian Raw Steel Process*, which has been very elaborately described by Professor Tunner, may be taken as a type of these processes. The hearth employed is about 3 feet square and 9 inches deep. The sides are formed of cast-iron plates, and the bed of stamped charcoal and ashes about 6 inches thick. The height of the back plate facing the twyer, and on which the pig iron to be melted lies, is adjustable, so as to be from 2½ to 5 inches above the twyer. The twyer is about 1¼ inch diameter, and projects about 4 inches over the plate, pointing downwards at an angle of 10° to 16°. The pressure of blast is equal to 15 or 16 inches water column. Charcoal is the fuel used. The pig iron is first refined by melting it down, and subjecting it more or less to the action of the blast, by which it is decarburized and the silicon removed. While this melting and refining action is going on, the previously-formed crude lumps of steel are heated and worked in the same fire. By the waste of metal in this operation a good deal of rich cinder is formed, which reacts upon the refined iron lying in the hearth. If the refined iron is still liquid, rich hammer slag is poured in. When sufficiently refined, the slag is removed, fresh charcoal put in, and the lump of metal raised up among it, so as to be more under the action of the blast. In this way the carbon is reduced to a sufficiently low point, and the mass then sinks down into a pasty cake at the bottom of the hearth. The cinder is then tapped off, the cake removed, and the adherent, semi-fluid metal knocked off. The cake is then cut up, and forged under the hammer. The process takes from five to six hours.

Fig. 1.



Production of Steel from Wrought Iron by Cementation.—This mode of making steel has been carried on for 150 years in England, and similar plans have been followed in Sweden, Westphalia, and other countries; but when and by whom the discovery of the process was made is not known, its early history being involved in much obscurity. Reaumur, in 1722, speaks with great clearness upon the process, and even states that his own experiments showed, that if a bar of iron three-sixteenths of an inch thick took six hours to convert, a bar seven-sixteenths of an inch required thirty-six hours to become equally carburized, thus showing that not only was the process known, but the mode of action was being studied at this early period.

Fig. 1 is a vertical section of a converting furnace, *a*, *a*, are the converting chests; *b*, fire-place; *c*, ash-pit; *d*, *d*, arched roof; *e*, *e*, flues.

The process consists in exposing bars of wrought iron to the action of a prolonged heat while they are thoroughly embedded in charcoal, protected in such a way that the charcoal cannot burn. Under these circumstances, it is found that the bars take up a certain quantity of carbon, the amount depending upon the time of exposure and quality of the charcoal, &c. The carburization is found to proceed from the surface towards the interior, and as Reaumur showed a century and a half ago, it takes several times as long to convert a bar seven-sixteenths thick as it does to carburize to the same extent one only three-sixteenths thick. The mode of operation is as follows:—The bars of iron are placed side by side in a rectangular chest (*a*, Fig. 1), which is built up of fire-brick or freestone blocks. These chests are usually about 12 feet long, 3 feet 6 inches wide and deep, with walls 6 inches thick. They rest upon good solid masonry. Charcoal is spread upon the bottom, then a layer of bars, then a layer of charcoal about half an inch thick, then more bars, and so on till the chamber is filled, care being taken to allow for expansion of the bars lengthways and sideways. A thick layer of charcoal is placed upon the top, and the whole is covered with a plaster of "wheelswarf," four or five inches thick. This is the mixture of sandstone and steel which is produced by grinding steel on stones. A moderate heat renders it plastic, and thus it forms a perfect cover for the chests or "pots," and prevents the air from burning the charcoal. The pots are generally arranged side by side, with a fire-place beneath them, and from which flues pass up between and at the sides of the pots, so that the flame can thoroughly surround them. They are generally placed in pairs, and are covered by an arched roof, as shown in Fig. 1; and the whole is covered by a cone-shaped chimney. Trial bars are inserted in the chests in such a way that they can be drawn out and examined from time to time, to see how the cementation is progressing. When all has been carefully luted up so as to render the chests impervious to air, the fire is lighted, and the chests are kept at a good red heat for several days. Usually steel for melting, which must contain about 1 per cent. carbon, requires from nine to ten days; shear steel, which is less highly carburized, say to ¾ per cent., takes eight days; and spring steel, which requires from ½ to ¾ per cent. carbon, takes about seven days. When the proper amount of carbon has been taken up (judged of from the fracture of trial bars), the fire is allowed to burn out, or is withdrawn, and the pots allowed to gradually cool down. A usual charge for a furnace is from 16 to 18 tons of bars. When sufficiently cooled down the bars are taken out, and are found to have increased in weight from ½ to 1 per cent, and are frequently covered with blisters. Hence the product is known as "blister steel." The cause of these blisters was for a long time obscure, but it is now proved beyond doubt that they only occur in carburizing puddled

iron, and that they are due to the formation of comparatively large volumes of carbonic oxide gas, by the action of the carbon (taken up by the iron) upon the particles of slag contained in the puddled bar. The slag consists largely of oxide of iron, which becomes reduced thus, $C + FeO = CO + Fe$, and the carbonic oxide being given off more rapidly than it can be taken up by the iron, forces the soft covering into a blister. The theory of the process of cementation is not yet perfectly understood; but it is highly probable that the charcoal when heated produces carbonic oxide, and it may be cyanogen gas and hydrocarbons; and the iron when heated first occludes some of these gases and then decomposes them, in consequence of the affinity of the iron for carbon. Percy has clearly shown—1st, that carbonic oxide alone is perfectly capable of converting iron into steel; and 2nd, if pieces of iron be heated in charcoal, under conditions in which it is difficult for carbonic oxide to be generated, that the iron does not increase in weight, and is not converted into steel. Hydrocarbons are capable of producing carburization; but the many attempts that have been made to use them have not resulted in practical success.

The charcoal which has been used for one operation is found to be pulverized in a curious way, and after the process the dust is sifted out, and about an equal portion of new charcoal is added to the old before it is used again. Hard charcoal, rich in alkalies, is found to yield the best results, and this favours the view that cyanogen may do a good deal towards hastening the operation. Hence Tunner recommended the addition of a half per cent. potash and common salt to the charcoal. It is a curious fact that Blair has noticed that, in the reduction of iron ore by heating it in contact with charcoal in a reducing chamber, the presence of a small quantity of lime facilitates the elimination of oxygen from the ore, and Dodd shortened the time of cementing by using 6 per cent. lime and 2 per cent. soda. Coke powder does not answer in place of charcoal, probably on account of the sulphur which it contains; as there is little doubt that the tendency of sulphur is to prevent iron taking up carbon, and to throw it out of combination when it has been combined with iron.

The following complete analyses by Messrs. Pattinson and Stead will show the changes which take place in iron which has been subjected to the process of cementation.

SWEDISH BAR-IRON BEFORE AND AFTER CEMENTATION.

	Ⓒ		Ⓛ	
	Before.	After.	Before.	After.
Iron.....	99·298	98·571	99·660	98·699
Carbon, ...	·470	1·200	·220	1·210
Manganese,.	·120	·100	·044	·044
Silicon, ...	·037	·066	·052	·028
Sulphur,....	·035	·027	·016	·013
Phosphorus,	·032	·030	·008	·006
Copper,.....	·008	·006	trace	trace
	100·000	100·000	100·000	100·000

In commenting on these analyses Messrs. Pattinson and Stead remark, that "the small differences shown in silicon and manganese, in the bars before and after cementation, are due no doubt to slight differences in different parts of the bars, and not to any change having taken place." This is doubtless true, for it is well known that in puddled iron the slag is interposed very irregularly throughout the mass. On examining the above analyses, it will be seen that the only change has been the absorption of ·73 per cent. more carbon in the case of the sample of Ⓒ iron, and ·99 per cent. more in that of the Ⓛ sample. Both samples contain a rather large per cent. of carbon before converting, but particularly the first, which must be regarded as puddled steel. The Ⓛ iron is remarkably free from impurities. Much of this blister steel is used without further remelting, the bars being simply nicked and broken into short pieces, piled, heated, and forged into shape, when it is termed "shear steel." Frequently these bars are cut up again, repiled, heated, and forged again, when the product is known as "double shear steel." Blister steel is more readily welded than cast steel; but the welds are rarely perfect, and cutlery made from such steel can generally be detected by a practised eye by the marks of the welds. If a knife-blade, for instance, be examined carefully there will often be seen faint dark lines running parallel to the edge, owing to the wedge-shape of the blade revealing the layers of which the piece is made up.

Cutlery made from cast steel does not show these parallel striæ. Double shear steal is more liable to these marks than single shear, because in the first process it is customary to cover the pile with a clay wash to prevent oxidation while heating, and this adds to the difficulty of obtaining a perfect weld at the second operation. The heating of the piles is usually performed in hollow coke fires, and the welding under small tilt hammers, driven at great speed by water power. The kind of fuel used for heating the converting pots is one of considerable importance (it must be free burning, and leave no clinker), as is also the quality of the material from which the pots are made; and it was doubtless owing to the proximity of good water power, highly refractory materials, and first-class and cheap fuel, that Sheffield rose to be the Queen city of the steel manufacture. It seems curious that only Swedish irons were held to be capable of producing good cement steel, and that even of these one or two brands were considered infinitely superior to all others. But when we examine the analysis of the celebrated Ⓛ brand given above, we can see that few English brands, before hematite iron became so largely introduced, could be expected to yield so pure a product. There does not appear to be any reason now why Swedish iron should not be quite equalled by iron made from our own hematite pig. The following analysis shows clearly, that even in the pig iron the impurities are little more than in the Swedish bar, and with good puddling there is no reason why these should not be decreased to a very

considerable extent. Indeed, it is known that with mechanical puddling even very impure pig iron can be purified to a far greater extent than was possible by hand-puddling, and that practically all the sulphur and phosphorus can be eliminated.

Sample of the West Cumberland Company's No. 1 Hematite Pig made from Best Cumberland Ores:—

Iron,		94·341
Carbon,	Combined,	·440
	Graphitic,	3·300
Silicon,		1·537
Sulphur,		·019
Phosphorus,		·032
Manganese,		·331
Copper,		trace.
		100·000

Crucible Steel.—The art of melting steel in crucibles is due to the industry and acumen of a member of the Society of Friends, Benjamin Hunstman, of Handsworth, near Sheffield, who perfected the invention about the year 1740 It is stated on good authority that Hunstman was a mechanician of no mean order, and well versed in other kindred subjects. Some accounts state that he was a watchmaker, and that the trouble he met with from the irregularity of the metal of which watch springs were then made, induced him to look about for a means of improving the steel. Whatever may have induced him to turn his attention to the subject, it is certain that he succeeded in a wonderful way in building up a new industry under very unfavourable circumstances; for before his time there was neither furnace that would melt steel, crucible that would hold the molten metal, nor ingot moulds into which to pour it, and he succeeded in so perfecting the manufacture as to leave it very much in the state in which it is at present practised in many

Fig. 2.

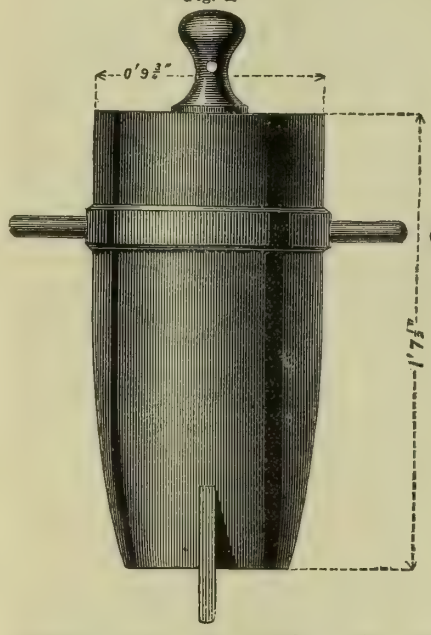


Fig. 3.

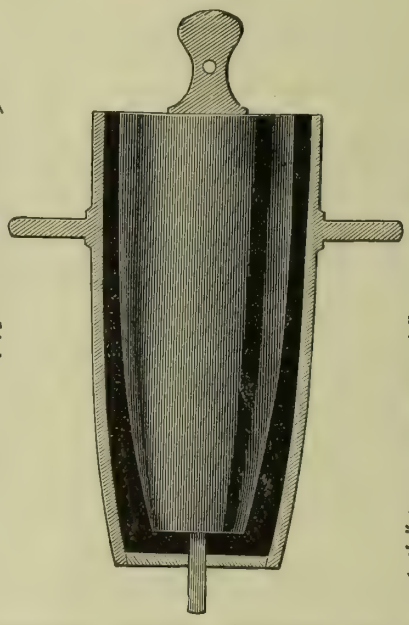
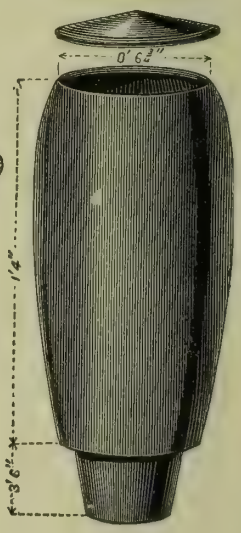


Fig. 4.



Sheffield works. He carried on the manufacture as a secret process for a number of years, and Hunstman's steel became of world-wide reputation. It is popularly believed that the secret of its manufacture was gained by stealth, and the story is well told in a very able article on steel in the work entitled "Useful Metals and their Alloys."

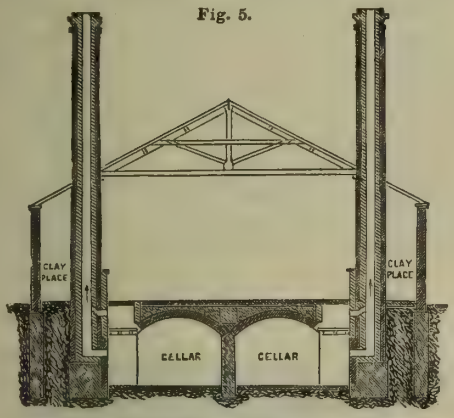
The material formerly employed for crucible steel was invariably the cemented steel just described. The bars were nicked and broken into small pieces, which were then placed in a crucible already heated to a bright white heat in a small coke furnace. Now it is not at all uncommon to use unconverted bar iron, and also scrap of all kinds from the Bessemer process, but all carefully broken and assorted in a "mixing house" under skilled control; the dearer Swedish iron being used only for the very finest steel.

The crucibles were formerly made from the highly refractory Stourbridge clay alone, or mixed only with a small quantity of coke dust. Afterwards more local clays were found that answered equally well, and for many years past still more refractory (although more tender) crucibles have come into extensive use, made of a mixture of clay and plumbago. The apparatus for making crucibles is shown in Figs. 2, 3, and 4, and the general method of manufacture will be easily understood. The well tempered clay is weighed out in lumps of the size to make one pot. The lump is rolled up and thrown into the well-greased mould (Fig. 2), which has a close iron bottom with a small hole in it. A hard wood plug (Fig. 3), of the shape of the interior of the pot, having an iron pin in the bottom and an iron knob on top, is then driven into the clay until the pin centres itself in the hole of the false bottom of the mould. This keeps the plug in the centre, and spreads the clay evenly around to the shape of

the mould. The plug is withdrawn, and the top part having been trimmed and loosened from the mould by passing a knife between the clay and mould, it is placed upon a short pillar which pushes up the false bottom and sets the clay free. The pots are then very slowly and carefully dried, and gradually annealed before use. They are taken hot from the annealing furnace to the melting furnace, where they are placed upon small lumps of similar material to keep them off the bars of the grate. Covers or lids of fire clay (Fig. 4) protect the contents of the pots from the fuel in which they are heated.

The old form of crucible furnace was of very simple construction, and is represented below (Figs. 5, 6); as is also an improved coke furnace (Figs. 7, 8) used at Vickers, Sons, and Co's., and figured in Hackney's valuable paper on Steel in the "Transactions of the Institute of Civil Engineers," vol xlii., 1874–75. E. Reynolds, who furnished Hackney with these drawings, says—"I have failed to find either here or amongst our neighbours any drawing of the

Fig. 5.



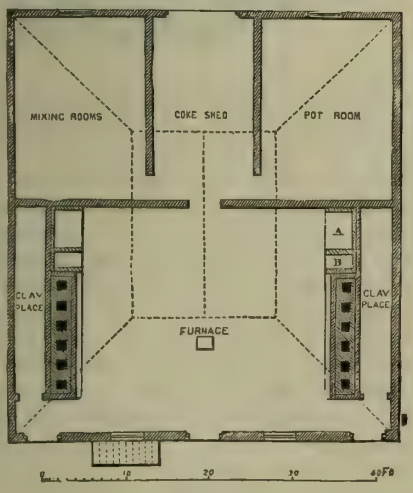
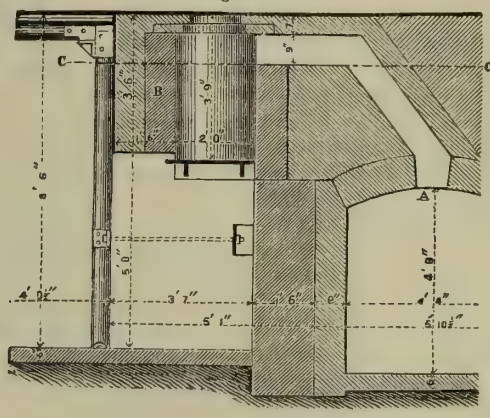


Fig. 6.

conventional furnace. It differs from ours chiefly in the following particulars, viz.:—Whereas it is customary to carry the products of combustion of each furnace direct into a flue, forming a chimney 14 inches square and about 40 feet high, we, having to combine the contents of many crucibles into one large casting, and wishing to avoid the obstruction of these chimney stacks, have connected many melting holes into one common flue, with a chimney outside the building. Next, whereas common practice covers the 'cellar' by a brick arch of from 10 to 15 feet span, beneath which the pots are made, we have made iron floors, and make the pots in a separate building.

Fig. 7.



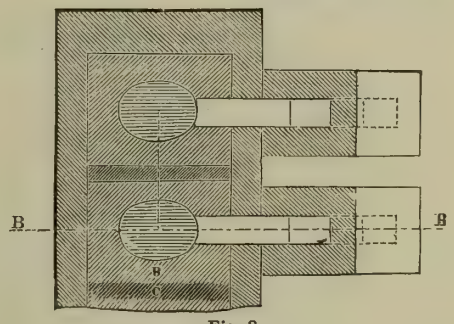


Fig. 8.

"In England, I believe universally, the practice is to use two pots in each melting hole, and the ordinary charge for each pot is 50 lbs. for the first round; but we, having succeeded in producing very good pots, commonly use 70-lb. pots, and on special occasions have used pots containing 100 lbs. The ordinary day's work (in Sheffield) is three rounds, the charges being about 48 lbs. in the first round, 44 lbs. in the second round, and 30 lbs in the third round; whereas we get about 66 lbs., 60 lbs., and 50 lbs., respectively. The diminished charges in the second and third rounds are due to the corrosion of the inside of the pot, at the level of the melted metal, from the action of the slag, technically called 'flux,' which lies on the surface of the metal, and which so far reduces the thickness of the pot that it would not be safe to fill it so full a second time.

"The first round takes about four hours to melt, the second three hours, and the third from two to three hours, according to the temper of the steel

melted; easy work being preferred for the third rounds.

"Abroad, at any rate in the large German works I have seen, the practice is to use four pots in each melting hole, these being of inferior quality and thrown away after each round. This, however, sacrifices the heat due to getting the pot hot and ready for work, which makes an hour difference between the first and second rounds.

"The consumption of fuel may be taken at about $3\frac{1}{2}$ tons of coke to the ton of mild steel, and from $2\frac{3}{4}$ to 3 tons for other qualities; the general average being about 3 tons per ton of steel.

"Before altering some of our melting holes to the Siemens system, we had 336 ordinary melting holes, and when very busy we used about one-half night and day; so that we used more than 1000 crucibles daily, each turning out about $1\frac{1}{2}$ cwt. of steel, so that the daily production was about 75 tons. In altering to the Siemens system we get the same melting power in the same space; *i.e.*, Siemens furnaces for ninety-six pots occupy the same space as forty-eight old melting holes, which number was our set for one chimney, but, as a matter of course, the Siemens furnaces ordinarily work night and day, so that the turn-out, if fully employed, would now be greater; the continuous work being found so destructive to the ordinary furnaces that it could only be used exceptionally."

The following particulars were supplied by Dr. SIEMENS, of the working of regenerative gas furnaces for crucible steel melting:—

"February 27, 1872.—The Monkbridge Iron Company report that their consumption of coal per ton of steel melted amounts to 2·9 cwts., which includes the gas necessary for annealing the pots.

"January 26, 1875—Messrs. SANDERSON Brothers report that their men make sixty-six hours and a half each set per week, work being commenced at one a.m. on Monday morning, and ceasing at from 1 to 3.30 p.m. on Saturday. The men change shifts every twelve hours—viz., 6 a.m. and 6 p.m., those coming at 1 a.m. on Monday leaving at 6 a.m. the same day: three casts of tool steel are made per twelve hours, and sometimes seven per twenty-four hours, according to the temper of the steel melted.

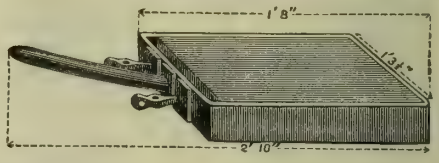
"February 22, 1866—Messrs. VERDIÉ ET CIE (Firminy, Loire) report to M. BOISTEL that they make one cast in three and a half to four hours, say six in twenty-four hours. The pots last six casts, instead of three as in the coke holes. The consumption of coal is about 3 tons per twenty-four hours, and the steel melted 2·7 tons, equal to 1·11 ton of coal per ton of steel melted.

"Statement of the working of a regenerative gas steel-working furnace at the works of Messrs. ANDERSON, COOK, & Co., Pittsburg, Pa., from 7th to 14th November, 1869:—Twenty-four heats, averaging three hours and a quarter each, produced 43,013 lbs. of steel, and consumed 26,448 lbs. of coal, or 348 bushels (of 76 lbs. each). Total cost of fuel, 348 bushels at 3 cents = 10·44 dols.

"In the old furnaces at the same establishment, it takes to melt the same weight of steel 5160 bushels of selected coke at 10 cents, making the total cost for fuel = 516 dols. Thus the saving effected by the gas furnace, in fuel alone, amounts to 505·56 dols. on 43,013 lbs., or 19 tons English, or 26·50 dols. per ton. The melting is done in plumbago pots."

The general process of manipulation in making crucible steel may be described as follows:—The crucibles, as stated above, only last for two or three meltings. They are carefully annealed and gradually raised to a red heat, ready for the steel-melter when he begins his day's work. If coke fires are used the stands of fire-clay are placed upon the bars, the fire lighted, and when this has burnt up two pots are placed side by side in the furnace with their lids on. Small pieces of coke, about the size of a hen's egg, are then filled into the furnace around the pots. When the furnace and pots are at a good white heat the charge of steel, which may be 60 lbs. to begin with, is put into the pot thus:—The steel in small pieces is held in a small iron shovel by the assistant. The melter then rapidly draws the cover (Fig. 9) off the furnace, lifts

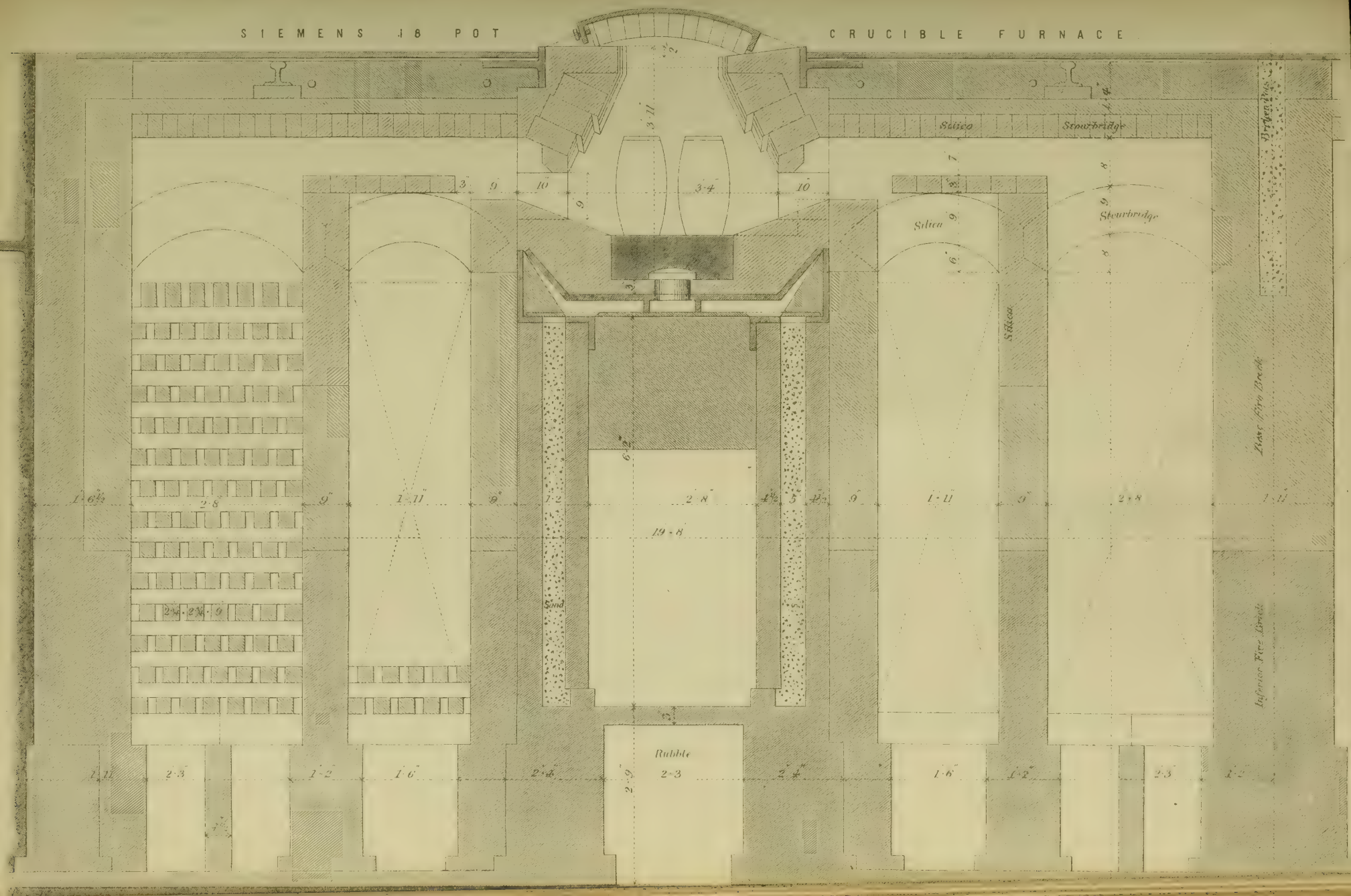
Fig. 9.



the crucible lid, and places the iron funnel (Fig. 10) in the pot, while the assistant shoots the pieces of metal gently down the funnel into the pot, where they are levelled by an iron rod and the crucible cover put on. The other pot is served the same way, and then the coke-fire is made up, and the grate bars cleared; more coke is put on from time to time until the charge is melted, which generally takes from about two to three hours. After the metal has all become fluid, it is usual to allow it to stand molten in the pot, and keep the heat up for about half an hour to "dead melt" the steel, as the workmen term it. What this dead melting consists in is even yet somewhat doubtful, but it is highly probable that BESSEMER's explanation is correct as far as it goes. What is known is that if the metal be poured into a mould as soon as melted, it is very fiery, that is, gives off a number of sparks while being poured, and produces an unsound or honeycombed ingot; while if the metal be kept molten in the crucible for some time, until the surface shows a brilliant and still face, and it is then poured, it runs quietly into the mould and the ingot shrinks on cooling, the bulk of it being perfectly solid. The top portion is found to be piped, or has a hole down the centre, but this is broken off and remelted. BESSEMER supposes that when first melted the metal contains no silicon, but that by keeping it molten the carbon of the metal reduces some of the sand that was put into the crucible to fill up the hole left in the bottom during the process of manufacture, and that silicon is thus set free and alloys with the metal, producing thereby

STEEL.

SIEMENS 18 POT CRUCIBLE FURNACE



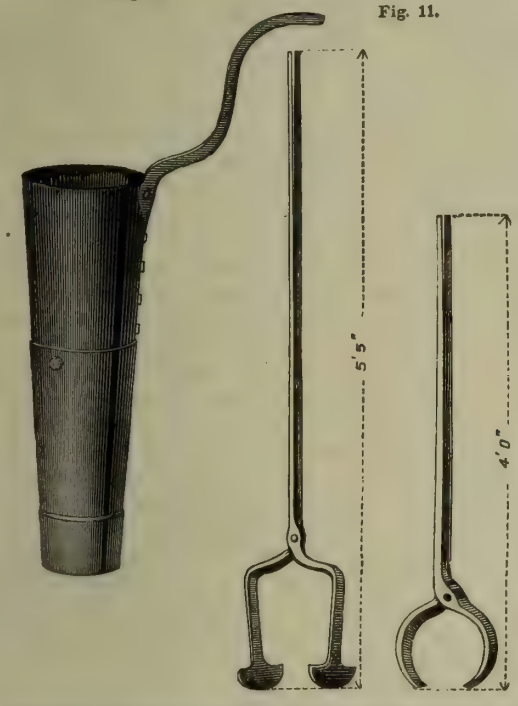
a more solid steel. It is true that the quantity of silicon found in the steel is very small, but this may be no measure of the quantity which may have been reduced, as a double reaction may go on as follows:—

$$SiO_2 + C = CO_2 + Si.$$
$$Si + 2CO = SiO_2 + 2C.$$

In this way the carbonic oxide, which is known to be occluded in large volume in the steel and is almost

Fig. 10.

Fig. 11.



certainly the cause of unsoundness, may be got rid of, and hence when dead melted the metal will contain no gas and will run solid. This question will be touched upon again further on.

The metal having been "dead melted" has next to be teemed. This is a delicate operation, and requires a good deal of skill. The moulds are usually made of cast iron in halves, which are bound together by a hoop and wedges, after the inner surfaces have been well coated with a layer of soot from burning tar. They are placed slightly inclined in a small pit in the floor. The steel melter, having enveloped his legs in several layers of sackcloth well steeped in water, stands straddle legged across the furnace, and with the tongs, *a* (Fig. 11), grasps the crucible securely, lifts it quickly from the furnace, and deposits it into the "teeming hole" close behind him. The bottom of this is covered with coke dust, to prevent the cooling of the crucible. The lid is then removed, and the clinker which may have gathered round the crucible is cut away with a long chisel-shaped bar. The melter then grasps the pot around the middle with the teeming tongs, *b* (Fig. 11), and gradually pours the steel down the centre of the mould, while an assistant keeps back any scoria that may be floating on the surface with a "flux stick," which is simply an iron rod on the end of which a lump of tenacious hot slag has been accumulated. When the pot has been emptied the lid is put on, and it is returned to the furnace preparatory to receiving another charge; one melter takes charge of six holes or twelve pots. The second charge is made lighter than the first, so as to lower the slagging line in the pot, for it is found that the pots eat away most along the level of the fluid steel, owing to the corrosive action of the floating slag. With good pots a third charge can be obtained, but they sometimes give out at this point, and the steel is lost by running through the fire into the ash pit. It is very remarkable that steel which has thus run through the coke fire, called "slag" or "runnings" by the workmen, is found to have taken up so much sulphur as to render it unfit for the finer purposes, and it has therefore to be utilized for common steel castings, &c. The steel sets almost instantly in the small moulds used for cutlery and tool-steel ingots, which are about 3 inches square. The hoops are, therefore, knocked off at once, the ingots removed and taken out into the open air to cool. The tops are then broken off down to the bottom of the piping, and if the steel has been dead melted it is found to show a peculiar radiated structure, the lines of crystallization running at right angles to the cooling surfaces.

If heavy ingots or castings are to be made, the contents of a number of pots have to be poured into one mould. Sometimes this is done direct—that is, without the use of an intermediate receiver; and in this case the men have to be very expert, so as to keep up a *continuous* stream of metal from a great number of pots. The pots are brought up in rapid succession, two men carrying a pot between them in a pair of two-handled tongs; generally, however, where large castings are to be made, an iron receiver, lined with loam, is placed over the mould. This has a hole in the bottom, stopped by a fire-clay plug on the end of a loamed-up iron rod, which is lifted when the metal is to be poured. The rude valve above described is kept closed till the contents of several pots have been run in. The valve is then lifted, and as the metal runs out, crucible after crucible is teemed into the receiver, which is never allowed to get empty till the mould is full. If the casting is large, the metal will continue to sink in the mould for some time, and fresh steel is added to make up for the shrinkages.

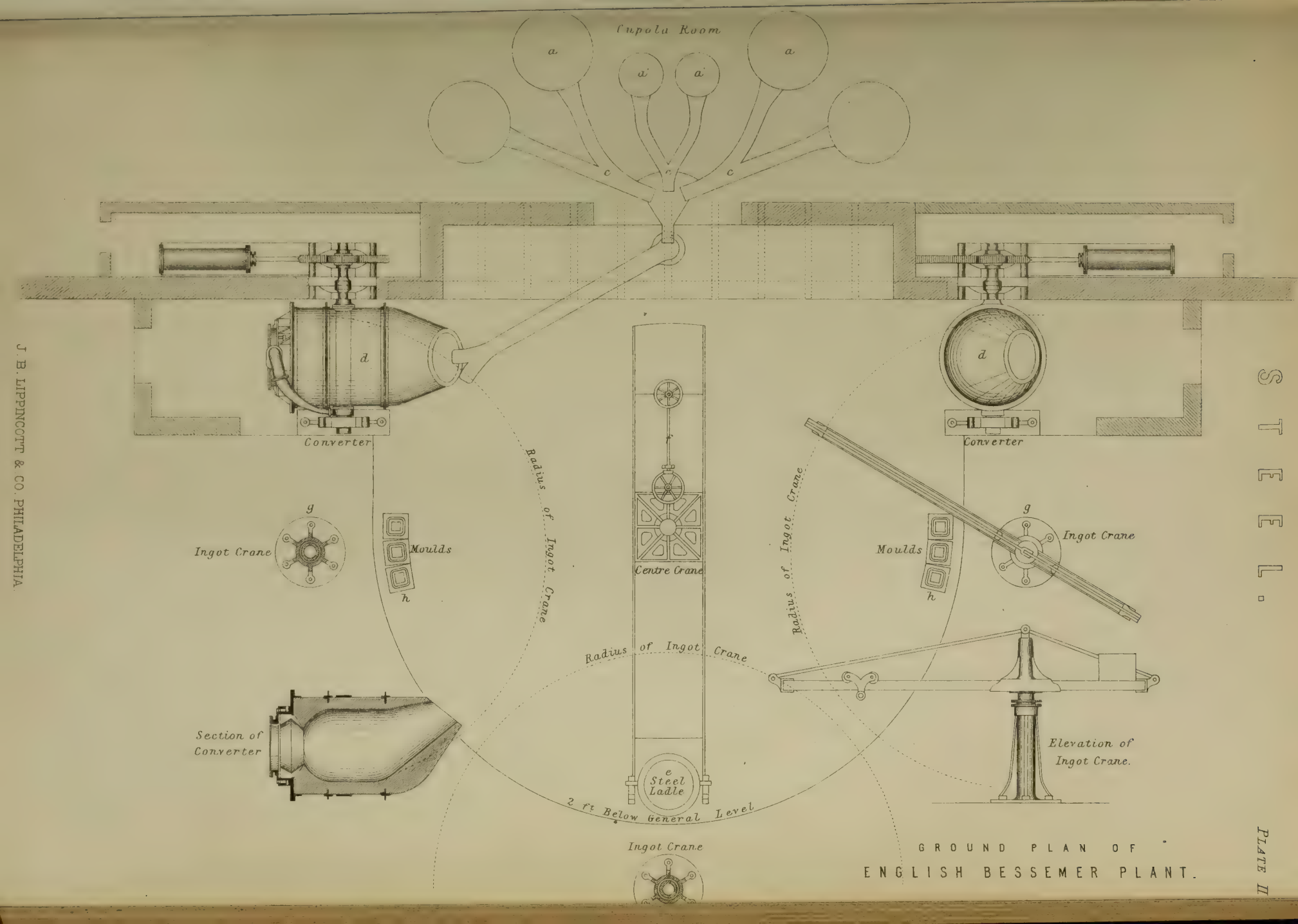
Although David Mushet had patented "the melting of malleable iron in the form of bar or scrap, or iron ore, when sufficiently rich and pure, in crucibles, *with a proper per cent. of carbonaceous matter*," in the year 1800, and had well described the process in his celebrated treatise on iron and steel—thus clearly showing, what indeed was well known from the Indian process of making wootz, that at a high heat iron in the fluid state was capable of taking up carbon—yet most of the steel made in crucibles was produced from cemented bar before

the time of Heath. In 1839, however, Josiah Marshall Heath took out a patent for the addition of manganese to steel in the crucible in the form of "carburet of manganese," which he made by submitting black oxide of manganese and carbonaceous matter to a very high temperature. This material was for some time sold as Heath's powder; but he himself afterwards showed his agent that it was not necessary to form the carburet by a *separate operation*, and that the same result would be attained by simply putting the mixture of oxide of manganese and carbon into the crucible with the steel. Advantage was taken of this deviation from the wording of the patent to ignore its legality, and one of the most remarkable patent trials on record was the result. The story is pathetically told by Charles Dickens in *Household Words*, to which the reader is referred. The discovery made by Heath of the power possessed by manganese to produce good steel out of moderately inferior iron led to a largely increased manufacture; and his plan is still followed very extensively, although his oxide of manganese and carbon are now giving place to R. Mushet's spiegeleisen and ferro-manganese. Since the invention of the regenerative system by Dr. Siemens, his plan of gas furnaces has largely superseded the old coke fires for crucible steel melting. Plate I. shows a vertical section of a Siemens crucible furnace of the most recent kind, as erected by Murdock, at the Steel Casting Works, Barrow. Whereas the old coke furnaces used 2½ to 3 tons of coke to melt 1 ton of steel, not more than 1½ ton of coal is required for the same work in the Siemens producer.

The Bessemer Process.—No metallurgical discovery has been more pregnant with benefit to the world in general, or more profitable to its author, than the invention which is now universally known as the *Bessemer process*. Although it is little more than twenty-two years since Bessemer first made his tiny experiment with about 25 lbs. of metal in a small crucible, and less than twenty years since he explained to the Institute of Civil Engineers his complete plans for working the process on a commercial scale, so rapid has been the growth of the manufacture that it is estimated that in the year 1877 over *two million tons* of steel were actually made by the Bessemer process. Estimating this at only £5 per ton in the *ingot*, we have the enormous sum of £10,000,000 sterling as the value of the raw steel produced by this process in one year—the actual value of the finished articles being about double this amount. Or to put the matter in another light: there are at the present time close on 350 Bessemer convertors in existence. Assuming the plant in connection with and dependent upon each of these to have cost on an average £20,000 (which is a moderate estimate), we find that something like £7,000,000 sterling have been invested in works for carrying on the Bessemer process and finishing the articles produced from it, while there are probably no less than a quarter of a million workpeople engaged in the various branches of the manufacture.

Bessemer's first experiments were made on a small scale at his Bronze Manufactory in London, where, in order to test his ideas regarding the refining of iron by blowing air *through* it, he had a small crucible furnace constructed; and after melting about 25 lbs. of pig iron in a crucible, he passed a clay pipe into the metal, and forced a current of air through it for some time. The result was that he blew out or wasted about half his material; but the remaining half proved to him conclusively that if air was blown upward through molten iron instead of merely *on to* its surface, as in the old Welsh refinery, much greater refining action was produced. His aim was to produce, if possible, an improved metal for guns. Having satisfied himself thus far, he took out his first patent, dated October 17, 1855:—"Improvements in the manufacture of cast steel," in which he proposed to use crucibles placed in a rectangular furnace, with the fire bars at the side instead of at the bottom. Each crucible was to have a tap hole in the bottom, through which the metal was to be tapped into a mould beneath at the proper time. Steam or air, or both, were to be forced through a pipe to the bottom of the pig iron, which was to be run into the hot crucible in a fluid state. The invention was tersely described as consisting in "forcing currents of air or of steam, or of air and steam, into and among the particles of molten crude iron, or of remelted pig or refined iron, until the metal so treated is thereby rendered malleable, and has acquired other properties common to cast steel, and still retaining the fluid state of such metal, and pouring or running the same into suitable moulds." The inventor distinctly states that "steam cools the metals, but air causes a rapid increase in its temperature, causing it to pass from a red to an intense white heat."

On December 17 of the same year, Bessemer obtained a further patent for blowing the air up through the molten iron, which was to be contained in a *spherical or egg-shaped vessel of iron, lined with fire-brick, and suspended upon axes;* and when the process had been carried far enough, the metal was to be poured from the vessel into moulds. This arrangement is clearly the first germ of the idea of tipping the vessel on axes to discharge the fluid iron, instead of tapping it through a hole in the bottom of the crucible; but in this apparatus the single blow-pipe carrying the air downwards to its escape orifice was still retained. Later on, however (May, 1856), we find Bessemer patenting an upright fixed cylindrical vessel, with several twyer-pipes permanently fixed into, and forming part of the lower lining of the vessel. This form of converting-vessel has been extensively adopted in Sweden for working small charges of metal; but it has been found in practice on larger quantities of metal, that the operation of opening the tapping-hole was one of great difficulty and delay, and not unfrequently caused a charge to be over-blown and spoiled; because the blast was necessarily continued so long as the metal was retained in the vessel. In this arrangement the blowing operation was also neces-



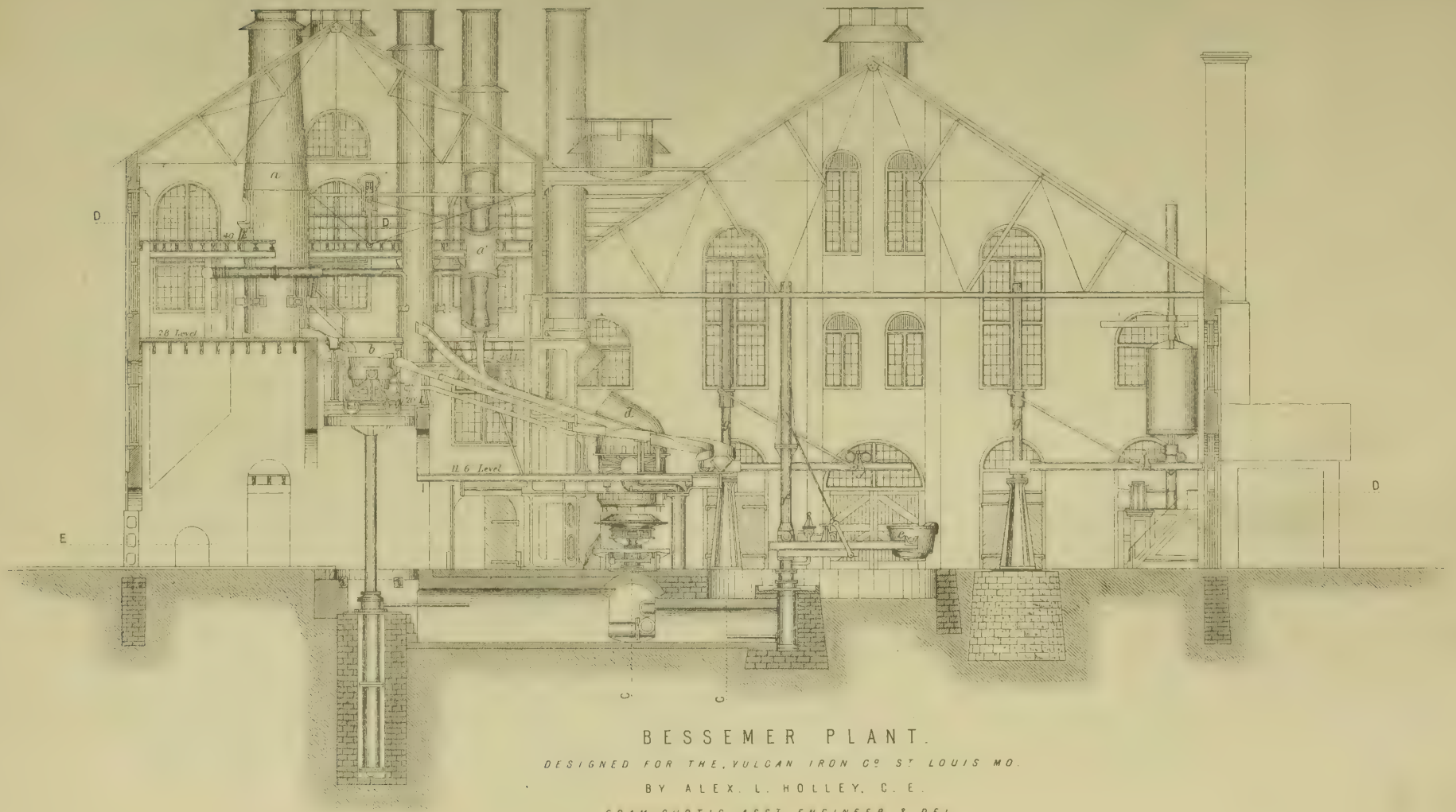
GROUND PLAN OF

ENGLISH BESSEMER PLANT.

STEEL.

PLATE II

J. B. LIPPINCOTT & CO. PHILADELPHIA.



BESSEMER PLANT.

DESIGNED FOR THE VULCAN IRON Co. ST. LOUIS MO.

BY ALEX. L. HOLLEY, C. E.

GRAM CURTIS, ASST. ENGINEER & DEL.

SECTION AND ELEVATION ON A. A.

SCALE

J. B. LIPPINCOTT & CO. PHILADELPHIA

sary during the whole time that the crude metal was being run into the vessel, in order to prevent its entering the twyers. These disadvantages were of themselves well nigh fatal to the commercial working of the process. To remedy these defects, Bessemer designed that peculiar-shaped vessel mounted on axes, now so well known as the Bessemer "convertor." This vessel has numerous fixed twyers evenly distributed over the bottom of it, and the peculiar form of the vessel allows it to be put in such a position that the crude metal may be run into it, without rising up to and covering the twyers; so that after all the charge has been run in, it may be turned quickly into an upright position, when the twyers will become immersed below the fluid, and the whole charge be thus operated upon simultaneously, instead of portions of it being blown from the first commencement to run in the metal, as was the case with the fixed vessel before described; and so in like manner, at the desired moment, the process is made to cease by a reverse movement of the vessel, which brings the orifices of the twyers again above the level of the metal.

This movement of the vessel on axes, and its peculiar form, afford also great facilities for getting rid of the fuel used in the first place to heat it, and for discharging the converted metal and the scoria after the operation; it also enables the workmen to obtain safe and ready access to the twyers, while the shower of cinders and flame emitted during the operation is directed into a chimney, and conveyed away.

The extreme irregularity in the weight to be moved during the different positions which the vessel occupies, and the difficulty of conveying motive power to it by the ordinary appliances of drums and straps, &c., is entirely overcome by the application of a hydraulic cylinder, the piston-rod of which is joined to a rack, and gears into a toothed wheel fixed on the axis of the convertor, the power being controlled by a lad stationed at a convenient distance from the heat and splashes of the apparatus. Novel and important as is the invention of converting crude molten iron into steel in a few minutes, without human skill or manipulation, it is perhaps more than equalled by the novelty and ingenuity displayed in devising an apparatus so well adapted to carry out the peculiar requirements of the original intentions on a grand commercial scale.

It is curious to observe how greatly accidental circumstances sometimes modify the course pursued, and the results obtained in experimental research. The quality of pig iron which Bessemer happened to purchase for his early experiment contained so little sulphur and phosphorus, that most encouraging results were obtained; indeed, some of the first experimental ingots made by him in London were successfully rolled into flanged rails at Dowlais, from ingots 10 inches square, without either the employment of spiegeleisen or the process of hammering previous to passing them through the rolls. This early success caused Bessemer to very much underrate the injurious effects of sulphur and phosphorus, so plentifully found in common pig iron; indeed, he appears to have taken it for granted that these elements would all disappear under the influence of the excessive temperature generated in his process.

Bessemer rightly divined that by blowing air into the molten metal the carbon and silicon would be eliminated; and he found that by the combustion of these elements alone, the metal would be raised to a temperature sufficient to maintain malleable iron in a state of perfect fluidity; but he was entirely in error in supposing that the sulphur and phosphorus would be driven off by excess of temperature, and hence all attempts to convert the lower qualities of pig iron by his process has hitherto failed.

The success attained up to this time was very remarkable; and there is no wonder that the reading of the paper by Bessemer at the Cheltenham meeting of the British Association on 13th August, 1856, which he described as "On the Manufacture of Malleable Iron and Steel without Fuel," produced a startling effect upon those engaged in the manufacture, and that several of those most largely interested were anxious to secure the right to make iron and steel in such an apparently economical manner. Indeed, such was the anxiety of a few leading men to acquire an interest in the patent, that within twenty-five days of the reading of the paper "licenses to manufacture malleable iron under the patent were purchased by iron-masters to the extent of £25,000."

An unprejudiced observer, reading the paper of Bessemer at the present time, cannot but be struck with the clear manner in which he had grasped the subject, and a perusal of the whole paper will well repay the reader.

The following analysis of the first Bessemer steel rail, kindly furnished by E. Williams, will be read with interest. The carbon is much lower, but in other respects it is remarkably like an analysis of steel made by the Heaton process, analyzed by Snelus, and recorded in the Iron and Steel Institute Proceedings, and is in fact a phosphorus steel. Williams states that "the steel rolled uncommonly well."

Analysis by J. E. Stead of the first Bessemer steel rail rolled at Dowlais in 1858:—

Iron,	99·300
Carbon,	·081
Manganese,	trace.
Silicon,	trace.
Sulphur,	·139
Phosphorus,	·446
Copper,	none.
	99·966

Although Bessemer had succeeded thus early in producing material of most remarkable quality, it must be admitted that there was still a degree of uncertainty in stopping the operation at the right point to produce the harder qualities of steel; while if the softer varieties, approaching in character to wrought iron, were to be made, it became necessary still to employ the finer varieties of Swedish cast

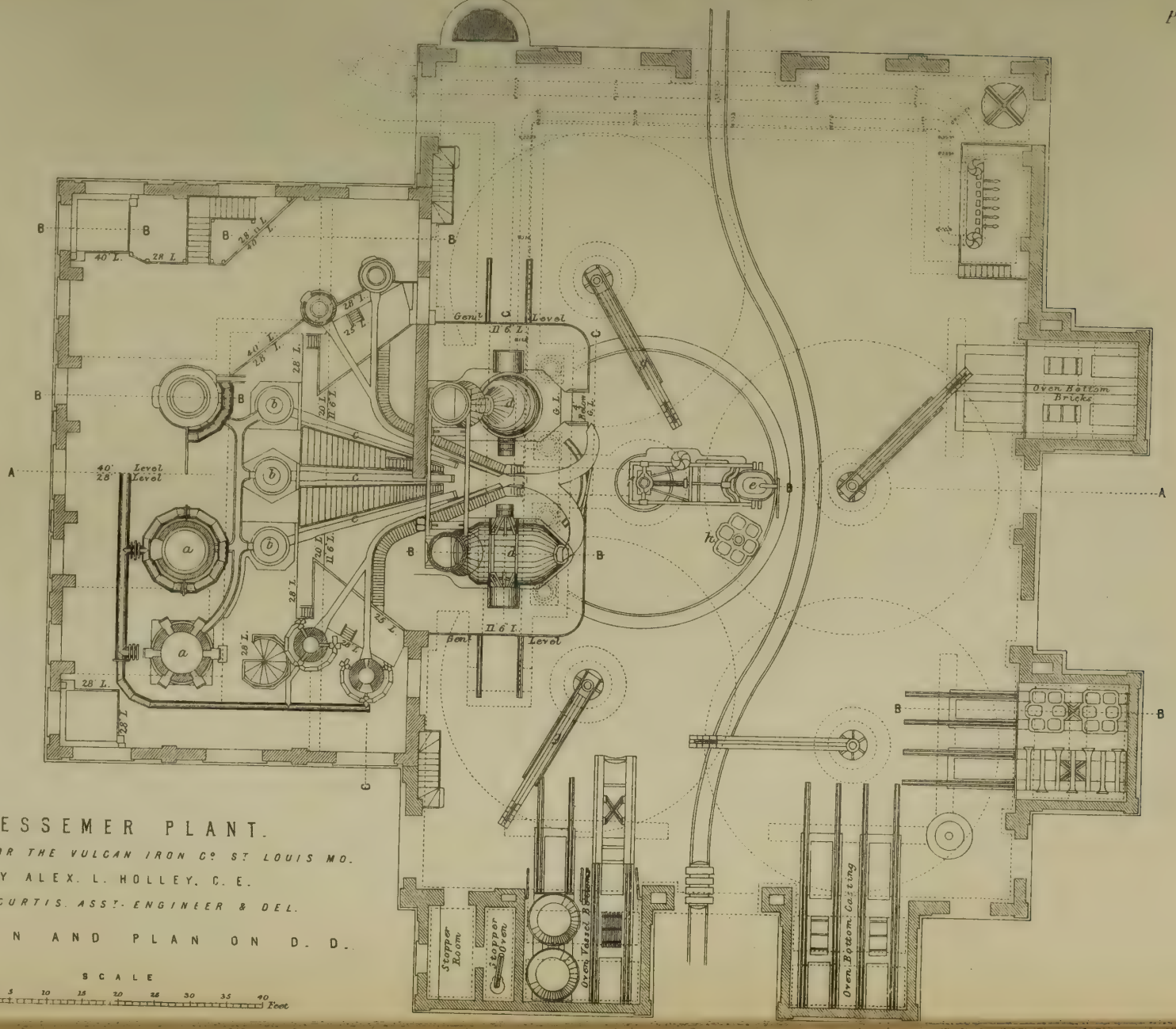
iron, since if all the carbon were blown out of even hematite English iron, the remaining metal was highly red-short. Swedish pig iron contained less silicon than English hematite, while it contained also from 2 to 4 per cent. of manganese. Hence it required less blowing, and when the operation was finished there still remained some manganese to counteract the excess of oxygen required; and the softer products when made from Swedish iron were thus found to work well.

The effect of manganese upon steel was pretty well known at the time of Bessemer's invention, in consequence of the discoveries of Heath; but the idea of applying the manganese in the form of a metallic alloy is due to Robert Mushet. He patented (September 22, 1856) the addition of molten Spiegeleisen to the decarburized Bessemer metal, for the double purpose of restoring a fixed quantity of carbon and adding manganese to the product, and it was this addition to Bessemer's invention that made it perfect; and Mushet's plan of completely decarburizing the metal, and then adding a known quantity of carbon, is now almost invariably followed. Unfortunately for Mushet, his patent right was allowed to lapse through the non-payment of the third year's duty, and his invention became public property. This seems, no doubt, a great injustice to Mushet, but through the influence of Dr. Percy his claims received recognition from Bessemer.

Although little notice was taken of Bessemer's paper to the Institution of Civil Engineers, or of the remarkable specimens then shown, yet the process gradually made its way; and the success of the works which he and his partner erected at Sheffield (and in the management of which Mr. Bessemer enlisted the quiet talent of his brother-in-law, Mr. Allen), soon induced other Sheffield manufacturers to take it up; and first John Brown & Co., and then others, discovered that the manufacture of Bessemer steel was a profitable operation, as well as a wonderful metallurgical success.

The convertor used in the first instance by Bessemer, and then introduced into Sweden, where it has been constantly employed up to the present time, was a fixed vertical cylinder, lined with refractory material, and having horizontal twyers at the bottom, with a separate tap-hole. This was first thoroughly heated by fuel, the blast was put on, and then from 1 to 2 tons of molten pig run in. Refining commenced at once with an outburst of sparks, and frequent ejection of slag and some metal, the flame gradually increasing to dazzling whiteness. When the metal was assumed to be sufficiently decarburized, it was tapped into a ladle, and cast into ingots. After the invention by Bessemer of the movable convertor, the power of production was so greatly increased, that it became necessary to design an apparatus for dealing with large quantities of fluid metal, and removing the moulds and ingots with facility; and on January 8, 1862, Bessemer took out a patent for the employment of a pair of converting vessels, with a centre-casting ladle between them—the whole being moved by hydraulic power, and forming such an extremely practical and efficient set of apparatus for carrying on the process, that although very many clever men have since done their best to improve upon these plans, the essential portions are retained in the most approved plants of the present day. In 1863 the plan of having duplicate bottoms removable from the vessel, so that they could be got ready beforehand, was introduced, but it did not find general favour for many years; and the improvement of this portion, by so arranging the parts that the joint between the old lining and the new bottom could be made from the outside, was due to A. L. Holley, of the United States, who took out his English patent in 1870. Holley's plan of replacing the bottom and the lengthening of the vessels, so as to prevent the metal and slag being blown out, which was first introduced by Pink of Hoerde, are probably the greatest improvements that have been made in the Bessemer apparatus. Plate II. shows the arrangement of Bessemer plant of the most approved English fashion; and Plates III. and IV. show the elevation and plan of one of the most recent arrangements, as designed by Holley for American works. The reader will thus be able to see the points of difference in the practice of the two countries—*a a* are cupolas for melting pig iron; *a'*, spiegel cupolas; *b*, receiving ladle; *c*, runners for molten metal; *d*, convertors; *e*, the steel casting ladle; *f*, centre crane; *g g*, ingot cranes; *h*, ingot moulds. The English plan is mainly followed on the Continent. It will be observed that an essential point of difference lies in the arrangement of the convertors. In the English plan, as designed by Bessemer, they are placed face to face, and only little more than half the circle traced by the casting ladle can be used for placing moulds. In the American system the two vessels are placed side by side, and thus leave about four-fifths of the circle available for moulds. This so facilitated the work of casting and removing the ingots, &c., that a considerably greater number of casts could be dealt with in a given time; and thus while in English practice 350 tons of ingots per week was considered a good output from a pair of vessels, the Americans were getting 500 or more. But this large output was only rendered possible by increased facilities at other points, and of these Holley's "dry bottom," as it has been termed, and the use of an intermediate receiving ladle for collecting and weighing the metal from the cupolas and holding it ready for the convertors, are two of the most important.

In the earlier practice it was deemed necessary to remelt the pig iron in reverberatory furnaces, on the ground, that if melted in a cupola, the iron would become deteriorated. This continued to be the practice for a long time, entailing great waste of fuel (as it required from 9 to 10 cwts. of best coal to melt 1 ton of iron), and also of the iron itself. It is somewhat doubtful who first proved that this expensive melting was unnecessary; the merit of having first used iron melted in a cupola being claimed both by the late George Brown, of Sir J. Brown & Co., and also by John Birch, of the



BESSEMER PLANT.

DESIGNED FOR THE VULCAN IRON Co ST LOUIS MO.

BY ALEX. L. HOLLEY. C. E.

GRAM CURTIS. ASST. ENGINEER & DEL.

SECTION AND PLAN ON D. D.

SCALE

Ins. 12 0 5 10 15 20 25 30 35 40 Feet

Railway Steel and Plant Co. The latter gentleman read a very interesting and able paper on "Bessemer Steel" before the Association of employers, foremen, and draughtsmen of the mechanical trades of Great Britain, in 1868; and in this paper he makes the following statement:—

"It was usually the custom to melt the pig metal used for conversion into Bessemer steel in air or reverberatory furnaces. Now this is a costly and wasteful way of melting iron for this purpose. There is an opinion prevalent amongst engineers generally, that by the melting of pig iron in air furnaces it is improved thereby. For foundry purposes it undoubtedly is, but for our use it is not; it is very much deteriorated. The air furnace, as you are all aware, is purely an oxidising furnace; that is, the metal, after it is melted, is subjected to a current of heated air passing over it continually, and, as a matter of course, is continually being oxidised from the moment of its first melting until it is tapped out; it is consequently much wasted, and the yield of steel is therefore proportionably less. In case of accidents in the after part of the process, such as a disabled vessel or any disarrangement in the pit, the waste of metal is still going on in the furnace. I have seen cases of this sort where not more than 50 per cent. of the iron has been got out at tapping, and what has been got out was utterly useless for conversion. But the loss of iron is not the greatest evil in this case. You will remember I told you that it is requisite that the metal used for this process should contain graphitic or free carbon; now, the action of the air furnace not only oxidises the iron, but it also burns off the carbon, the very fuel required for the conversion of the cast metal into steel. To put it in other words, it refines it too much, and takes out what we require to raise the temperature of the metal to such a pitch as to keep it fluid when in the state of pure iron; of course this deterioration is only in proportion to the time it is exposed to this oxidising influence, but under the most favourable circumstances there is always a deterioration. Early in the year 1865 I suggested to the directors and manager of the Railway Steel and Plant Co., Newton Heath, the feasibility of melting our metal in a common cupola; it met with much opposition, and, I assure you, some very learned arguments were used against it by outsiders; and some people who ought to have known better, said that if we began we should never have a good heat. This was at the commencement of our operations at Newton Heath, and though thoroughly convinced of the practicability of the thing, I rather chose to get our materials into the market by the old method of melting, than meet at once the direct opposition which the novelty had excited in a commercial way. By the permission of the managing directors, I had 3 tons melted in our foundry cupola, brought liquid in a ladle, and poured into the convertor, made the heat in the usual way, hammered it into blooms, broke one or two of them; when the gentlemen above referred to, who had expressed their belief that we should not get one good heat, saw them (without knowing that they had been made by the use of the cupola), they said they were the finest samples they ever saw. The matter was very soon settled; we erected two cupolas on Woodward's steam jet principle, and we have not used the air furnace since. The Mersey Iron and Steel Co. were the next to adopt it, and now it is in general use both at Sheffield and elsewhere. The cupola possesses many advantages over the air furnace; the first cost is not near so great, and the maintenance for the number of tons of iron melted is considerably less; the cost of melting is greatly reduced in the article of fuel, and there is little or no waste of iron in remelting. But the greatest thing in its favour is the ease with which we are enabled to remelt all steel scrap cuttings and chippings of every kind. It is the complete cure for the scrap difficulty, which has for so long a time been a great drawback to this process. It is next to impossible to remelt Bessemer scrap in the air furnace, on account of its oxidising action, and the small amount of carbon which the scrap contains; while in the cupola we have not the least difficulty, because of the reducing * action of the furnace, and the material being surrounded with carbonaceous matter in a high state of combustion."

Repeated experiments by Snelus and others have shown that good grey iron can be remelted in a cupola with good coke if a small portion of limestone be added to the charge, without risk of taking up sulphur. It has also been thoroughly demonstrated that during this process of remelting some silicon — generally from one quarter to one half per cent.—is removed from the iron; and it is the opinion of Snelus that the improvement in tenacity which Fairbairn found as a result of several times remelting the same grey pig iron was due to this removal of silicon. On the other hand, white iron, or iron poor in carbon and free from manganese, does certainly take up sulphur on remelting it in a cupola. There is always a small trace of phosphorus present in coke, and doubtless this is mostly taken up by the iron during remelting; so that by performing the operation a great number of times, as Fairbairn did, there is a point reached at which the iron begins to deteriorate. And this was exactly what he found by his mechanical tests. But the chemical analyses of some of these samples, which were made by Calvert, do not appear to support these conclusions. The analytical results, however, as will be seen from an examination of the figures given below, are so remarkable that it is evident that they are *not reliable*, and it is desirable that they should be repeated.

The pig was No. 3 Eglinton, hot blast, remelted in a cupola with coke. Three test pieces, 1 inch square and 5 feet long, were taken with each cast, and they were broken on supports, 4 feet 6 inches apart, by a centre load. The experiment was continued up to the eighteenth remelting, and samples from the first, eighth, tenth, and eighteenth remelting were analysed by Calvert.

* The reducing action in a cupola is very slight.—Ed.

TABLE I.

No. of Remelting.	Specific Gravity.	Transverse breaking load, 1 inch section, 54 inches apart.	Mean Ultimate Deflection.
			Inches.
1	6·969	490·0	1·440
8	7·025	491·3	1·753
10	7·108	566·9	1·626
18	7·385	312·7	0·479

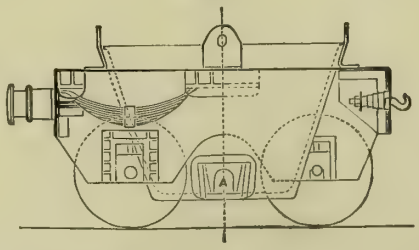
CHEMICAL ANALYSES.

No. of Remelting.	C.	Si.	S.
1	2·76	·77	·42
8	2·30	1·75	·60
10	3·50	1·98	·26
18	3·75	2·22	·75

The use of the cupola for melting the pig is not only a great saving, but also facilitates the work, by turning out a greater quantity in a given time.

Within the last four years even the cupola has been superseded, and manufacturers have to a large extent found it possible to carry out BESSEMER'S original idea, and take the metal in a molten state from the blast furnaces to the convertor. The merit of first practically carrying this out successfully with movable convertors, is due to the talented management of the Terre Noire Works, France. Generally it is not possible to place the convertors so near the blast furnaces that the metal can be run direct from one to the other. An intermediate ladle is therefore necessary; and as it usually has to travel over some distance, it requires to be mounted on a carriage. The ladle may either be tapped, as at Dowlais, or tipped and the metal poured at once into the vessels, as at West Cumberland Works. Both plans have their merits, the tipping being quickest done and requiring no runner for the metal; the tapping cuts the vessel lining out less, and allows less slag and scurf to enter the vessel. In both plans a single ladle has carried over 1000 tons of cast iron without requiring relining. Fig. 12 is Dowlais' tapping

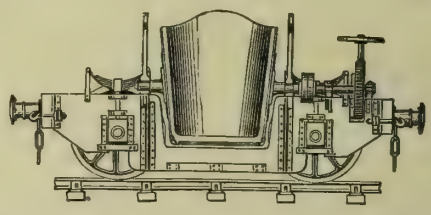
Fig. 12.



ladle; A is the tap hole: Figs. 13 and 14 show the arrangements of the West Cumberland tipping ladle. Three ladles and carriages at West Cumberland Works have now carried about 80,000 tons of molten metal in the last two years, with scarcely any repairs beyond relining with bricks and loam, and they appear to be capable of doing duty for some years longer.

The recent improvements in English Bessemer plant consist in making the casting pit shallower, in some cases doing all the work upon the level ground

Fig. 13.



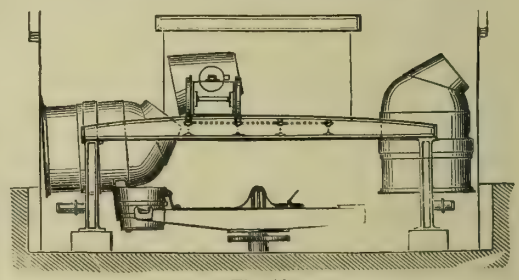


Fig. 14.

(although in the writer's opinion this latter plan is a doubtful advantage), and in increasing the radius of the casting crane so as to make room for more moulds. With larger and shallower pits there is now no difficulty in making considerably over 1000 tons of ingots per week in a pair of vessels in England; but this is still far behind the best American practice. The greatest output from a pair of vessels that has been recorded up to the present time, has been that of the North Chicago Steel Works, under FORSYTH, recorded in *Engineering*, March 22, 1878. The following are the particulars:—Blowing began every Monday at 6 A.M., and work was over for the week on Saturday at 5 P.M., sometimes much earlier. No work on Sundays, except ordinary repairs:—

1st heat turned up Tuesday, January 1, at 6 a.m.
1372nd heat blown Friday, February 1, at 5·30 a.m.
Product of ingots for—

					Tons.
5 Days	ending	Saturday,	January	5,.....	$1489\frac{890}{2240}$
Week	"	"	"	12,.....	$1797\frac{1248}{2240}$
"	"	"	"	19,.....	$1738\frac{410}{2240}$
"	"	"	"	26,.....	$1767\frac{1202}{2400}$
4 Days	"	Thursday	"	31,.....	$1307\frac{400}{2400}$
			Total for Month,.....		8100

Turns worked, 50.
Average product per turn,..... 162
Heaviest 12 hours' work, 30 heats,..... 176
Lightest " " 25 " ..... $144\frac{1802}{2240}$
Average life of bottoms used during month, 13 heats.

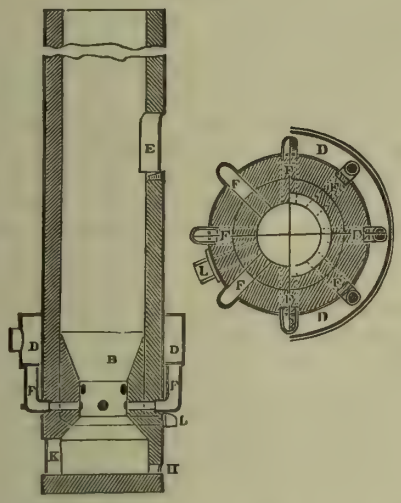
These results were obtained from a single pair of 5-ton convertors. The above steel was chiefly rolled into rails, of which the mill made during the month $6247\frac{1}{2}\frac{5}{2}\frac{5}{4}\frac{0}{0}$ tons "first class," the "second quality" amounting to 1·9 per cent.: ninety-three men and boys were actually employed in the Bessemer department, of following nationalities:—

Germans and Bohemians,	43·00
Irish,	27·96
English,	16·13
Norwegians,	8·60
Americans,	4·30
	99·99

The Essential Parts of a Bessemer Plant for conducting the process according to present modes of workng are :—

1. *The Cupola.*—Fig. 15 represents an ordinary English cupola, with a double row of twyers. Blast main, D D; charging door, E; twyer pipes, F F; tapping hole, H; cleaning door, K; slag tapping

Fig. 15.



hole, L. It will be seen to consist of a wrought-iron casing, lined with firebrick. The bosh or constricted part around the twyers is further protected with a lining of ganister, rammed in a semi-plastic state around a core, in order to withstand the excessive heat at this point, which is the zone of fusion; there is a charging-hole at the top, and the portion of the cupola above this point serves to conduct away the waste products of combustion. There is a *double* row of twyers in order to increase the melting zone. The twyers are connected with the blast main, from which they can be shut off by a slide valve. It is advisable to have a hole through the twyer, by which a bar can be introduced to clean away any slag that may accumulate at the nose of the twyer. About 12 inches below the twyers there is a tap-hole for the slag, which is allowed to run off continuously as soon as it rises to this point; and the lower portion of the cupola is enlarged to form a well, which is made sufficiently large to hold one charge of metal, generally about 8 tons. The charging of the cupola is now frequently carried on continuously, and the metal is tapped off as soon as it rises to the slag-hole. Formerly the full charge of metal, with its equivalent of coke, was put into the cupola, and melted down before another charge was introduced, in order to keep the charges separate, and insure the proper quantity of iron. In practice this can be kept sufficiently accurate by measuring the quantity as explained above.

There is an aperture left in the casing of the well, about 2 feet square, through which the residue can be raked out at the week's end, or when the cupola has to be put out for relining. This is made up with bricks and clay, which are retained by an iron door, after the fire has been lighted in the cupola. In starting a cupola a good fire of coke is first formed in the well, and when it has thoroughly burnt up, and is red-hot up to a little above the twyers, a bed of about 1 cwt. of coke is put in at the charging-hole, and then a layer of broken pig iron, then more coke with a little limestone as a flux, then more pig, and so on till the cupola is full. The blast is then put on, and as the charge sinks, more coke and iron are thrown in. The quantity of coke used varies very much. In the best practice, about $1\frac{1}{2}$ cwt., or rather less, suffices to melt a ton of iron; usually, however, the quantity employed is 3 cwts. or even more. This waste of coke is generally due to having too short a column of material from the charging-hole to the twyers, so that the whole of the heat of the ascending gases is not absorbed by the descending material. A good deal of useful combustible gas, carbonic oxide, escapes unburnt from the top of the charge, and several plans have been attempted for burning this among the charge at the top of the cupola. This endangers the regular working of the cupola, by tending to produce what are called scaffolds. These are generally produced by the half-melted pigs soldering themselves together across the cupola, and leaving little or no passage for the ascending gases.

Alexander Wilson has devised a better plan of utilizing the gases, by burning them on the top part of the cupola, and using the waste heat to raise the temperature of the blast, by causing it to traverse a spiral cast-iron pipe placed in the top of the cupola above the charging-door. Cooper heats the blast for the cupola by passing it through a cast-iron hot-blast stove, placed in the chimney above the Bessemer convertor. In America, instead of raking the remaining coke and slag out of a door in the side of the cupola, a movable bottom is employed, which is dropped down after a few casts (eight or ten) have been run. In English practice it is possible to get 6800 tons melted in a cupola, before putting it out for repairs.

The spiegeleisen is melted in a smaller cupola, having generally only two or three twyers, but similar in other respects to the pig-iron cupola. Various plans are adopted for raising the blast for cupolas. Root's blowers have found great favour in England, and Mackenzie's in America; but probably the cheapest and best are either high speed fans, or simple direct-acting blowing engines with large blast-cylinders, where first outlay is not material. When the charge of iron has been melted, it is in England run down channels in sand at once into the vessels. In America the metal is run into an *intermediate ladle* holding about 12 tons. This is placed on a weighing machine, and thus at any

moment the exact charge of iron can be poured into the converter. This is a very useful addition to the ordinary Bessemer plant, as it saves much loss of time, and insures greater regularity in the weight of the charge. In America the channels for the pig iron, or "runners," are made of iron grouted with clay wash, and are much steeper than in the usual English practice. This saves scrap, and gets the iron more quickly into the vessels.

Convertors.—These are pear-shaped vessels of boiler plate, generally about 8 feet diameter by 15 high, carried on trunnions, and capable of being turned up or down by a strong rack and pinion wheel, the rack being fixed to the end of a piston rod working into a hydraulic cylinder. The convertors are lined with ganister, which is a siliceous rock of a peculiar nature. It appears to have been deposited in shallow seas just after the millstone grit, and before the permanent land surfaces were formed upon which the bulk of the coal-measure plants grew. Professor Hull has endeavoured to identify this bed over a very large area, and there is little doubt that it will ultimately be found in many districts in which at present it is supposed to be absent. It occurs very largely in the Yorkshire coal-field, and also in Lancashire, Shropshire, South Wales, and has lately been discovered in the Newcastle coal-field; but the finest quality of ganister stone is found around Sheffield, at Penistone and other places. It there forms the underclay of a thin coal seam, and is very largely worked, particularly by Mr. Lowood, for exportation to all parts of England, and even to Austria and Russia. The following analysis will show its chemical composition:—

ANALYSIS OF GANISTER STONE.

Silica,	97·50
Alumina,	1·20
Lime,	1·23
	99·93

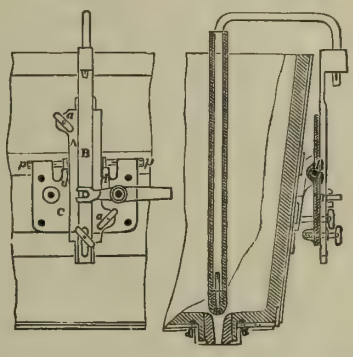
Analysis is, however, only a partial guide to the value of a material of this kind, for it is found that the peculiar value of this Sheffield ganister depends more upon its physical characters than its chemical composition. It appears to have been formed by the aggregation of extremely fine particles (produced from the wearing away of quartz rocks) of siliceous matter with a little alumina, which have then been subject to great pressure. It has a glassy or waxy fracture, quite different from all sandstones, and is extremely hard and tough. It contains numerous remains of plants, and often large masses of pyrites. It is not only highly refractory, but possesses the valuable quality of binding together like clay when ground fine and moistened. Sandstones, under these circumstances, are crumbly. It is the joint possession of these two properties that renders ganister so valuable for lining Bessemer convertors, cupolas, &c.

In lining the convertors a core of the shape of the interior is placed inside the casing, leaving an annular space, into which the ground ganister is rammed hard. To facilitate this work the converters are made in two or more parts, which are first rammed up with ganister, and then joined together by bolts and nuts. After making good the joints and inserting the bottom plug with its twyers, a small fire is lighted to dry it slightly, and then the vessel is half filled with coke and the blast kept on gently for about twelve hours. At the end of this time some rock salt is thrown in to assist in glazing the lining, and the vessel is then ready for use. With careful repairs at the end of each week one lining has lasted fifteen months of constant work, during which time about 15,000 tons of steel would be made in the vessel. The bottom of the vessel in which the twyers are set wears out very rapidly, lasting only on an average from eight to ten blows, and therefore requires to be constantly renewed. Formerly this was done by leaving the cast-iron frame in its place in the blast box, fixing the twyers in their places, and then ramming the semiplastic ganister around them from the inside of the vessel. This necessitated cooling down the vessel for each new bottom, and caused great delay, much wear and tear, and considerable expense in reheating the vessel again. Hence Holley designed the arrangement by which the bottom is made independently, dried in a stove, lifted into its place in the vessel, and the joint between it and the old lining made good *from the outside* by ramming ganister into the space. This plan answers admirably, and is used universally in America, but has never been fairly tried at any works in England, except the West Cumberland Iron and Steel Company's. At these works it has been in use for the last four years with very satisfactory results. Many attempts were made in England to insert a dry bottom in its place, and fill up the space between it and the vessel lining from the inside, by *pouring* into it a thin wash of ganister, or "slurry," as the workmen term it. For some time the plan failed to answer, but now it succeeds fairly well, and is in pretty general use in England. It has the disadvantage of being less secure than Holley's plan, and cools the vessel more. The plugs are, however, generally smaller, and a trifle more handy, than Holley's; but this is a matter of no consequence when proper facilities are provided for dealing with the latter. The twyers for carrying blast into the vessel are cylindrical plugs, of a mixture of three-fourths fire-clay, one-fourth ganister, perforated with a number of small holes about three-sixteenths diameter. The size of twyer, number per bottom, and number of holes, differ much in various works. In England the twyers have generally about thirteen holes, are from 18 to 22 inches long, 5 to 7 inches diameter at small end, and 6 to 8 inches at large end. From thirteen to sixteen are used in each bottom. They wear very irregularly; but a great deal depends upon the pressure of blast employed, and the column of metal which is worked upon them. It is very desirable to keep the pressure of blast up to 25 or even 30 lbs. per square inch. This keeps the metal out of the twyers and saves them much, for it is

found that the wear of the twyers is due far more to the following action than to mere fusion. On turning up the vessel, if the blast is weak, some of the metal runs part way down the holes in the twyers and there forms solid plugs, which cannot be blown out, but which gradually get oxidised in the twyer by the blast, the oxide so formed slagging away the siliceous material of the twyer; so that, looking into a vessel after a "blow," large black holes will be seen in many of the twyers, oftentimes rendering it necessary to replace them before the bottom is worn out. The number of blows obtained from one "bottom" varies much, in some works averaging only six, in others fourteen or fifteen: occasionally from twenty to thirty are obtained. The heavier the charge of metal, other things being equal, the shorter the life of the bottom. The blast is brought through one of the trunnions of the vessel into a box termed the blast-box, and the twyers are fitted into a cast-iron plate, forming the top part of this box. The box is closed at the bottom by a wrought-iron disc, which is fixed to the box by bolts and cotters, the joint being made air-tight by a ring of spun yarn steeped in clay wash. This bottom plate is thus easily removed for examining the twyers. The blast for the convertor is raised by a strong blowing engine, of a somewhat similar type to those used for blast furnaces, but proportionately stronger. The valves of the blast cylinders are usually of metal, and frequently of the piston type.

Casting Ladle.—When the steel has been made, it is poured into a large ladle, which is lined up with strong loam. This is carried by its trunnions, which are placed pretty near the centre of gravity of the full ladle, upon the end of a strong wrought-iron crane jib, the jib being carried upon the top of a hydraulic crane post. The top of this post is taper, and enters a corresponding cavity in a strong cast-iron centre-piece, to which the wrought-iron sides are bolted. A steel pin fixed into the top of the post enters a small steel cup in this casting, and centres and takes the weight of the frame, &c. About a dozen small steel rollers, fixed in a circular frame, run around the crane post and between it and the centre casting, thus enabling the top to turn freely on the post. Thus one man is enabled, by means of simple gearing, to turn the crane top and ladle around the post. The ladle has a hole in the bottom, and a small cast-iron ring is fastened to the bottom of the ladle, from the outside, by a couple of studs and cotters. In this ring is placed a fire-brick seat, having a hole through the middle about 1 inch to 1½ inch in diameter. In using a ladle for the first time, the seat is carefully luted up to the rest of the lining of the ladle; but as a seat only suffices for one cast, and the ladle lining may last ten or more, a new seat is put into the once-used ladle, thus:—The iron ring is taken off, and the new seat carefully fixed into it; ganister is then plastered around the top part of the seat, and it is forced up through the hole in the ladle and cottered into its place. The hole in the seat is closed by a plug on the end of a wrought-iron *stopper rod*. The rod is covered by loam or by *stringer bricks*, made in a pipe-making machine. This protects the iron *stopper rod* from the heat of the steel. The stopper rod is fixed to a slide, which works up and down in a guide attached to the outside of the ladle. By this means the aperture at the bottom of the ladle can be opened or shut at pleasure, the whole arrangement forming an ingenious valve. In England the stopper is set in its place by forcibly bending the rod; but Holley has designed a neat arrangement for adjusting the stopper mechanically—Fig. 16 is a front elevation; Fig. 17 is

Fig. 16. Fig. 17.



a side elevation; C is rivetted to the ladle. The swinging frame, A, that holds the stopper slide, B, is hinged at *d*. The pins, *pp*, are moved over these trunnions to hold them down in place when the frame is in use. When it is out of use the pins, *pp*, are slipped back, and the frame, A, and slide, B, are lifted bodily out and set into a fresh ladle. The stopper is adjusted by the set screw, *a a*.

When the steel has been poured into the ladle, the slag floats on the top; and on opening the stopper a stream of clear steel is allowed to run into the moulds.

The Moulds are usually of cast iron, and taper from bottom to top; so that when the steel has solidified, the iron "moulds" or "chills" can be lifted off, and the ingot of steel remains behind. The moulds stand upon a slab of cast iron, and a very rough joint between the mould and the iron slab or "bottom plate," upon which it stands, is sufficient to prevent the steel running out. At many works the steel is now run ascensionally, as it is termed. A number of moulds are fixed upon a bottom plate, in which are placed perforated bricks, connecting each mould to a central runner or "sprue." The steel is teemed down the central "sprue," and is distributed by the runner bricks to each mould, gradually rising in each till full. By this means cleaner ingots are formed, and the moulds last longer.

The movement of most of the apparatus of a Bessemer pit is produced by hydraulic power. This is found to be so much more steady than steam, and the apparatus generally is so simple, that direct driven gearing has entirely given place to it.

Ingot Cranes.—The moulds, ingots, and ladles

are lifted by hydraulic cranes, of which there are three types. Bessemer's, which is used mainly in England, consists of a strong cylinder casing fixed firmly to the ground, and having glands at the top and bottom. The ram is thicker at the top part than at the bottom, and the difference in sectional area is the active surface to which the power is applied. The jib is fixed to the top of the post, and is balanced by a heavy weight fixed to the opposite end. The American plan was designed by Holley. The ram works through a single gland in the top of the casing, and the whole sectional area is acted upon by the water pressure. Instead of being guided, as in the English plan, by the lower portion of the ram working in a casing, the post is carried above the jib and is stayed from the roof of the building. Messrs. Tannett & Walker have recently introduced an ingenious arrangement for the purpose of balancing the weight of the moving parts upon the column of water in connection with the accumulator. For this purpose they employ two rams, one of which works in a casing which is in constant connection with the accumulator, to act as the balance for the crane posts, jib, &c.; the other is worked by a valve, the diameter of the second ram being only sufficient to give the power needed for the maximum weight to be lifted. A strong guide ram is also fixed to the crane head to insure stability. The arrangement works well, but requires very careful adjustment. A plan occasionally adopted is to fix the jib to the cylinder, and let it work on the ram which is fixed. This plan is only suited for special cases.

Hydraulic Pumps are of various kinds. Those by Armstrong are ingenious and scientific, but are always made with too short a stroke. There is nothing better than a good-sized ram with long stroke and very slow motion. Davey of Leeds has applied his differential valve gear to direct-acting pumps for high pressure with excellent results. Worthington's pumps, which are somewhat similar to Davey's, are used very largely in the United States.

The Accumulator, for regulating and storing the water pressure, consists of a large ram weighted on the top, and working in a strong casing through a well-packed gland.

Hydraulic Valves are a source of considerable trouble in steel works, and a really good balanced valve remains to be invented. Slide valves require great power to move them. Three and four way cocks leak rapidly, and require constant grinding. Luthy's valves, which are balanced, are ingenious and easily worked; but the leathers are a source of considerable expense in large works.

Present Mode of Conducting the Bessemer Process.—If the iron is to be taken direct from the blast furnaces to the convertors in a molten state, all that is necessary is to take care that it is of sufficiently good quality, that is, free from phosphorus and sulphur, and that it contains from $1\frac{1}{4}$ to 2 per cent. silicon if little or no manganese is present. The lower the percentage of silicon and manganese, the shorter will be the blow. Hence in Sweden five or six minutes often suffice to blow out sufficient carbon to leave the metal at the point of steel. In England it generally takes from fifteen to twenty minutes; but occasionally, when much silicon or manganese is present, the blow may last from thirty to sixty minutes. If the iron is remelted in a cupola, a proper system of charging must be adopted.

The old plan of arriving at uniformity in quality of iron was to have a number of brands, and by experiment to arrive at a mixture of these which worked well; a similar mixture being supposed to answer on all occasions. This was often found to fail, and the proper mixture had then to be found by experiment again. The more correct and scientific method which is now followed where the process is properly conducted, is to analyze beforehand the stocks of iron, and then to make up a charge from an examination of the analyses. With English pig iron it is generally sufficient to find the percentage of silicon, and to calculate the charge from this element. If the grade of the iron be not too low—say a fair mixture of Nos. 1, 2, and 3 Bessemer—a charge containing from $2\frac{1}{4}$ to $2\frac{1}{2}$ per cent. silicon is found to work well, as it blows sufficiently hot to leave no skull, and the silicon is not too high to endanger the quality of the steel by running the risk of leaving a variable quantity in the metal after the carbon has all been burnt out, or making the charge so hot as to cut out the moulds and bottom plates during teeming. Supposing, then, we have four stocks of iron, A containing 3·5 per cent. silicon, B 3 per cent., C 2·5 per cent., and D 1·5 per cent. If used alone, A would yield a steel that would be so hot as to cut the moulds on teeming, and the silicon would be so high that it would not all be burnt out by the time the carbon had been oxidised, and a siliceous steel would be the result. B would still blow hot, and there would be some risk of a siliceous steel. C would work well; but D would blow so cold that there would be insufficient heat developed to make the metal hot enough to remain fluid in the ladle during teeming, and there would be great risk of the whole charge consolidating in the ladle, forming a wasteful *skull*. But by mixing in the following proportions we get a charge that will use up all the samples without running any risk whatever:—

1 Ton A at 3·5,	3·5
2 Tons B at 3,	6·0
2 " C at 2·5,	5·0
3 " D at 1·5,	4·5
8	19·0
÷	
	Per Cent.
Average silicon,	= 2·37

The English method of converting is that devised by Mushet. The whole of the carbon is burnt out; and as English hematite contains little manganese, there is no difficulty in determining when this point has been reached, because the flame drops suddenly at this point. The change in *sound* alone is suffi-

cient to the practised ear to determine this point. The proper amount of carbon and manganese are then added by pouring into the vessel a certain quantity of molten spiegeleisen, or dropping into the vessel a known weight of ferro-manganese, if very soft steel is desired. When iron containing over 2 per cent. manganese is being blown, the point of decarburization is very difficult to ascertain by the flame test, and recourse has to be had to the slag and metal test. The carbon is known to be all blown out when the slag just begins to pass from a brown colour to a smoky black, and the globules of metal taken out with the testing pad flatten under the hammer without breaking. When very siliceous iron is being blown, the same test may be applied; or if manganese is absent, the colour of the smoke is a guide. While any quantity of silicon remains, the smoke will, as it issues from the convertor, have a grey colour; but when all the carbon and silicon have been burnt, it comes *out of the convertor* a deep, ruddy, brown colour, showing that combustion of iron is taking place. In making soft steel by the Bessemer process great care is needed to insure the thorough admixture of the ferro-manganese with the molten metal, so as to remove the excess of oxygen before the metal begins to set in the moulds, as otherwise very dangerous explosions in the moulds may take place. After the steel has been teemed from the ladle into the moulds, it must be instantly covered up, so as to solidify the top surface, and fastened down, unless an excess of manganese be employed or the steel be hard, in which case it will lie dead in the moulds, and not "rise" or "boil over," as the men term it. The iron moulds may be lifted from the ingots five or ten minutes after they are cast.

The Bessemer Process considered Chemically.—The following analyses exhibit the nature of the pig iron usually treated by the Bessemer process, and the changes which occur during the "blow":—

TABLE II.—ANALYSIS BY SNELUS, AT DOWLAIS, SOUTH WALES.

	Melted Charge of Pig.*	No. 1 Sample, taken at the end of first stage, 6 minutes from start.	No. 2, taken 9 minutes from start.	No. 3, taken at finish, before adding Spiegel, 13 min. from start.	Steel Borings from an Ingot.	Steel Borings from Rail Crop ends.
Iron,	94·682	97·245	—	—	—	—
Carbon, { Graphite,	2·07					
Carbon, { Combined,	1·20	3·218†	2·17‡	1·55	·097	·566	·519
Silicon,	1·964 / 1·941	1·952	·792 / ·798	·795	·635 / ·635	·635	·020	·030	·033
Sulphur,	·014	trace.	trace.	trace.	trace.	trace.
Phosphorus,	·050 / ·047	·048	·055 / ·058	·051	·064	·067	·055	·053
Manganese,	·086	trace.	trace.	trace.	·309	·309
Copper,	—	—	—	—	·039	·039

TABLE III.—ANALYSIS BY BARKER, AT ATLAS WORKS, SHEFFIELD.

	1.	2.	3.	4.	5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Graphite,	2·570	—	—	—	—
Combined carbon,	1·000	3·040	1·640	0·190	0·370
Silicon,	2·260	0·955	0·470	trace.	trace.
Manganese,	0·410	trace.	trace.	trace.	0·540
Sulphur,	0·107	0·091	0·098	0·093	0·090
Phosphorus,	0·073	0·070	0·070	0·070	0·059

TABLE IV.—AUSTRIAN WORKS, AT NEUBERG, STYRIA.

	1.	2.	3.	4.	5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Graphite,	3·180	—	—	—	—
Combined carbon,	0·750	2·465	0·949	0·087	0·234
Silicon,	1·960	0·443	0·112	0·028	0·033
Manganese,	3·460	1·645	0·429	0·113	0·139
Sulphur,	0·018	trace.	trace.	trace.	trace.
Phosphorus,	0·040	0·040	0·045	0·045	0·044
Copper,	0·085	0·091	0·095	0·120	0·105

No. 1, original pig iron.
No. 2, metal and slag taken at the end of the first period (six minutes).
No. 3, metal and slag taken at the end of the boil (twelve minutes).
No. 4, metal and slag taken at the end of the blow.
No. 5, metal and slag after addition of spiegel.

CORRESPONDING ANALYSES OF SLAGS FROM NEUBERG SAMPLES.

	2.	3.	4.	5.
	Per cent.	Per cent.	Per cent.	Per cent.
Silica,	46·78	51·75	46·75	47·27
Alumina,	4·65	2·98	2·80	3·45
Iron protoxide,	6·78	5·58	16·86	15·43
Manganese protoxide,	37·00	37·90	32·23	31·89
Lime,	2·98	1·76	1·19	1·23
Magnesia,	1·53	0·45	0·52	0·61
Alkalies,	traces.	—	traces.	traces.
Sulphur,	0·04	trace.	—	—
Phosphorus,	0·03	0·02	0·01	0·01

TABLE V.

	Iron used at Seraing for running direct into the Convertor.	Rail Steel made from same, without Spiegel.
Iron,	89·40	99·07
Carbon,	4·50	·32
Silicon,	2·25	·15
Sulphur,	·04	·04
Phosphorus,	·06	·07
Manganese	3·75	·35
	100·00	100·00

* This was the composition of the metal run into the convertor. It had been melted in a reverberatory furnace.
† The total carbon is estimated by direct combustion; the graphitic and combined by separate experiments.
‡ All combined.

TABLE VI.—ANALYSES BY ADOLF TAMM, AT WESTANFORS BESSEMER WORKS, SWEDEN.

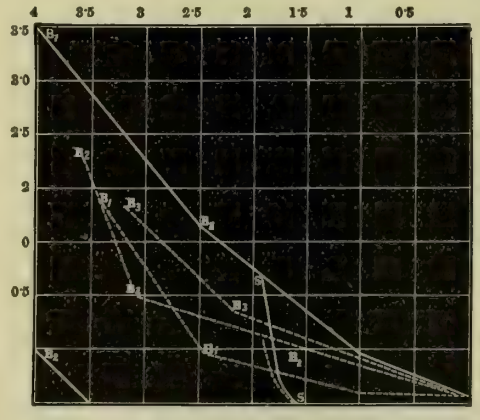
	Charcoal Pig Iron.	Bessemer Ingot.
Iron,	89·830	99·569
Carbon (graphitic),	2·15	—
" (combined),	1·95	·20
Silicon,	1·390	·033
Sulphur,	trace.	trace.
Phosphorus,	·015	·020
Manganese,	4·665	·168
	100·000	100·000

	Blast Furnace Slag.	Bessemer Convertor Slag.
Silica,	47·0	42·85
Alumina,	2·40	3·94
Iron protoxide,	·45	15·62
Manganese,	4·46	36·83
Magnesia,	18·10	trace.
Lime,	26·75	·70
Potash,	·62	—
Soda,	·41	—
Phosphoric acid,	·011	·015
	100·001	99·955

A consideration of the above analyses affords full information of the changes that take place in the metal during the blow. They show clearly that carbon, silicon, and manganese can be removed by the action of the blast, while phosphorus, sulphur, and copper are not removed.

The relative rapidity of oxidation of carbon, silicon, and manganese, in the Bessemer and Siemens processes, as deduced from the above and following analyses, are shown graphically in the accompanying

Fig. 18.



diagram, after Hackney. B_1, Neuberg sample; B_2, Atlas sample; B_3, Dowlais sample; manganese, white line; silicon, dotted line. The carbon per cent. is shown by the top row of figures. This diagram proves that the old notion, that all the silicon was burnt out before the carbon began to be acted upon, is not true. Manganese and silicon burn out rather more rapidly than carbon, for when the carbon has been reduced from 4 to 2·5 per cent. the manganese has been reduced from 3·5 to 1·6 per cent., and the silicon from 2 to ·4 per cent.; and in all these samples it is seen that, when silicon and manganese have been almost removed, there yet remains ½ to 1 per cent. carbon. The action is to some extent one of quantity; for if the silicon be much over 3 per cent. in English pig, free silicon will be left in the steel after all the carbon has been burnt out. Again, there is sufficient manganese in the Swedish and German iron to allow of a small quantity being left in the steel, to enable it to be worked when the carbon has been reduced to a low point.

Up to the present time all attempts to use pig iron containing phosphorus and sulphur for the Bessemer process have failed, because these elements persistently remain after the blow has been completed. Snelus believes that this is due to the fact, that in every case a strongly acid slag is formed, which is not favourable to the oxidation of sulphur and phosphorus, inasmuch as there is never any free base for the oxidised produce of these bodies to combine with; and hence he has patented the use of lime or limestone for the lining of Bessemer and other furnaces in which iron is treated, so as to be able to use a strongly basic slag, such as is obtained in the puddling furnace, as well as having the most refractory, and at the same time one of the cheapest materials, that can be used for the purpose. Experiments made some years ago have proved the truth of this hypothesis.

Composition of the Gases evolved from the Bessemer Convertor during the Blow.—A study of the nature of the gases emitted from the convertor cannot fail to throw light upon the process going on, and the following paper on the subject, read before the Iron and Steel Institute by G. J. Snelus, August, 1871, contains an exposition of this portion of the subject:—

The members of the Iron and Steel Institute will remember that Professor Roscoe, in his lecture on Spectrum Analysis, alluded to the difficulty of determining the cause of the greater part of the lines in the Bessemer spectrum, and pointed out that while the majority of observers referred them to carbon in some form, there were others who believed them to be mainly due to manganese. Assuming the lines to be due to carbon, it is clear that an analysis of the gas producing the lines would be a step towards solving the difficulty, since it would show us which condition of carbon we must refer them to. This is important, because we know that carbon, in different gaseous combinations and at different temperatures, produces, as Dr. Watts has pointed out, several distinct spectra.

Another question which suggests itself on examining the spectrum is that, supposing the characteristic lines are due to carbon, "How is it that the spectrum of carbon is not seen in the earlier stages of the blow, when an analysis of the metal proves incontestably that carbon is being burnt in considerable quantities from the commencement?"

It appeared to me that analyses of the gas at different stages of the blow might help to a solution of these problems; for though it is generally assumed that during the process of conversion the carbon of

the pig is burnt to carbonic oxide, this, as far as I am aware, has never been proved to be the case. It will be seen from the analyses that this turns out to be only partially true, and that the composition of the gases evolved affords us an insight into the nature of the process going on that could not be supplied by analyses of the metal and slag at successive stages.

The gas for analysis was collected by means of a long iron gas pipe, on the end of which a swan-neck trumpet mouthpiece of fire-clay was fixed, which was inserted in the neck of the convertor after it had been turned up. This generally got clogged up with slag during the experiment, and therefore served only for one blow. It was allowed to dip into the vessel, so as to be certain that no air could be drawn into the tube by induction. To the other end of the pipe glass tubes were attached at particular periods of the blow when the gas was required, and sealed up with the blow-pipe before being removed. A constant stream of gas was allowed to rush through the tube the whole time; and as this was done for two minutes before the first sample of gas was collected, it may be safely assumed that the whole of the air was swept out, and that the gas analyzed was a true sample of that produced by the direct action of the blast upon the metal and its constituents. It was found that during the first part of the blow the gas would not light at the end of the iron tube, but that from about the commencement of the "boil" to the end of the blow it burnt with the pale blue flame characteristic of carbonic oxide.

Samples of gas were taken every two minutes, and subjected to analysis with the subjoined results. The gases were analyzed in a modified form of the apparatus, described by Professor Frankland, for analyzing the gases incident to water analyses, which was found extremely convenient. Samples 3 and 5 were analyzed by different methods; the carbonic oxide in one case being estimated by absorption with a hydrochloric solution of sub-chloride of copper, and in the other by explosion with detonating gas and oxygen, and subsequent absorption by potash, after the method of Bunsen. It will be seen that the results agree closely:—

Sample 1.—This was taken two minutes from the start of a blow which lasted eighteen minutes. It contained—

Carbonic acid,	10·71
Oxygen,	·92
Carbonic oxide,	none.
Hydrogen (not estimated), Nitrogen,	88·37
	100·00

This I consider to be an unlooked-for result, because it is usually assumed that the carbon is burnt directly to carbonic oxide at all stages of the blow. Taking the nitrogen in this sample at 87 per cent., this corresponds to 23·05 volumes of oxygen. 10·71 volumes carbonic acid contain 5·35 volumes carbon vapour, which, referred to air as unity, represent 4·43 parts by weight of carbon. The carbonic acid contains its own volume of oxygen, which, deducted from 23·05, leaves 12·34 volumes = 13·62 parts by weight of oxygen, to combine with other elements than carbon. Now, ordinary English Bessemer iron contains little else for oxidation than carbon, silicon, and iron; the manganese being usually small in quantity, traces only of the sulphur disappearing, and the phosphorus remaining untouched. Of the three oxidizable elements, it is known from analyses of the slag that the iron is not burnt to any extent till towards the end of the blow, so that we have only to consider the carbon and silicon. The 13·62 parts of oxygen may, therefore, be assumed to be combining with silicon alone, so that as 32 parts of oxygen unite with 28 silicon, or in the ratio of 8 to 7, we have 11·91 parts silicon being oxidised at this stage, along with 4·43 parts of carbon; thus showing that, though both elements are being oxidised, it is the silicon which is disappearing most quickly. Now, this is exactly what an analysis of the metal proves, for a charge containing, on running into the convertor, 3·57 per cent. carbon and 2·26 per cent. silicon, was found by Barker in a few minutes to have lost ·53 per cent. carbon and 1·305 per cent. silicon. As an example of the nature of the gas evolved at a point between the times when this first sample was taken, and that obtained two minutes later, I give here analyses made by my friend W. Thorp, F.C.S., of the Rivers' Commission Laboratory, of two consecutive tubes of gas which I collected, four minutes from the commencement of a blow which, from the convertor being new, or the iron cold, lasted twenty-nine minutes—

	No. 1 tube contained	No. 2 tube contained
Carbonic acid,	8·94	9·296
Oxygen,	·916	·113
Carbonic oxide,	·078	·044
Hydrogen and nitrogen,	90·066	90·544
	100·000	100·000

Sample 2, taken four minutes from commencement, contained—

Carbonic acid,	8·57
Carbonic oxide,	3·95
Hydrogen,	·88
Nitrogen,	86·58
	100·00

It will be noticed that carbonic oxide is gradually increasing, while carbonic acid is decreasing in quantity.

Sample 3, taken six minutes from start, contained—

	By Absorption.	By Explosion.
Carbonic acid,	7·89	8·2
Carbonic oxide,	4·65	4·52
Oxygen,	absent.	absent.
Hydrogen,	—	2·00
Nitrogen,	87·55	85·28
	100·00	100·00

Dissecting these results, after the manner of those for No. 1, we find that 85·28 nitrogen correspond to 22·61 volumes oxygen. The carbon is combined with

10·46 volumes, leaving 12·15 volumes (13·42 parts by weight) of oxygen to combine with other elements. This will require 11·74 parts silicon, while the carbon going off as gas amounts to 5·27 parts. Carbon is, therefore, now being oxidised more rapidly in proportion to the silicon than was the case when No. 1 sample was taken.

Sample 4. This was taken ten minutes from the start, and as soon as possible after the boil had commenced. The complete spectrum was now visible and constant, and remained so to the end of the blow. The gas contained—

Carbonic acid,	3·58
Oxygen,	none.
Carbonic oxide,	19·59
Hydrogen (not estimated),	2·00 probably
Nitrogen,	74·83
	100·00

The great increase in the proportion of carbonic oxide, and corresponding decrease of carbonic acid, will here be noticed. This accounts for the increased luminosity of the flame at this period, as we have now a large volume of gas actually burning at the mouth of the convertor. Assuming all the oxygen now being evolved in combination to be derived directly from the blast at present passing through the iron, we have for the 74·83 volumes nitrogen, 19·84 volumes oxygen entering the convertor; but the carbonic acid contains 3·58 volumes, and the carbonic oxide 9·79 volumes; together = 13·37 volumes in combination with carbon, leaving 6·47 volumes for other work. This would oxidise 6·25 parts silicon, and there are 9·6 parts of carbon being burnt, so that the conditions are now reversed, carbon being oxidized at a more rapid rate than silicon. This is the point at which the carbon lines become well defined, and the analysis, we think, shows why this is so.

No. 5 *Sample*, taken twelve minutes from start, gave—

	By Absorption.	By Explosion.
Carbonic acid,	2·47	2·3
Oxygen,	absent.	—
Hydrocarbons,	absent.	—
Carbonic oxide,	29·58	29·3
Hydrogen,	—	2·16
Nitrogen,	67·95	66·24
	100·00	100·00

This sample of gas was specially tested for hydrocarbons, as being the most likely period of the blow to detect them, if they were formed to any extent. But although the gas was left in contact with fuming sulphuric acid for twelve hours, no absorption took place. As the results, by explosion, agree in showing the absence of these gases, I think we may fairly conclude that none are formed.

Sample No. 6 was taken fourteen minutes from start, and four minutes from finish of blow. It gave—

Carbonic acid,	1·34
Oxygen,	absent.
Carbonic oxide,	31·11
Hydrogen (not estimated),	2·00 probably
Nitrogen,	65·55
	100·00

The large percentage of carbonic oxide, and almost absence of carbonic acid, is remarkable. 65·55 parts nitrogen correspond to 17·37 oxygen. 16·89 volumes (= 18·66 parts by weight) are combined with 13·45 parts of carbon, leaving ·53 part of oxygen, which would combine with ·46 part silicon; so that at this point it is practically carbon alone that is being oxidised, the last traces of silicon disappearing very gradually.

Looking through these analyses, we note the broad fact that carbonic acid is formed in the first part of the blow with little or no carbonic oxide, while during the latter part carbonic oxide is formed with only traces of carbonic acid. The question "Why is this?" suggests itself. Why should the carbon take up twice as much oxygen at one time as another under apparently the same conditions? My own impression is, that both this chemical reaction, and also the difference between this carbon spectrum and that from carbonic oxide, under ordinary circumstances, are functions of temperature. It is certain that, at the commencement of the blow, the temperature cannot be much above a yellow heat, while at the end of the blow it is undoubtedly a good white heat. Now, it appears to me that, under the conditions in the convertor, carbonic oxide is the most stable body at a high temperature, and carbonic acid at a low one. This agrees with the experiments of I. Lowthian Bell, where he shows that the conditions of equilibrium for these gases in the presence of metallic iron are—

Low red heat,	150 vol. carbonic acid	For each 100 carbonic oxide.
Full red,	47 " "	
Approaching whiteness,	11 " "	

It also agrees with the general observation that, if the iron is cold when it comes from the melting furnace, the period of the boil is delayed; while, if the iron has been kept in a reverberatory melting furnace for a considerable time at a high temperature, this period is reached more quickly. The action of the oxygen upon the silicon may have something to do with the degree of oxidation of the carbon, for I find that the time when the boil takes place depends closely upon the quantity of silicon contained in the iron. Thus, with pig containing about 2½ per cent. silicon, the boil takes place about the middle of the blow, while with Swedish iron, which contains about only 1 per cent. silicon, this point is, I believe, reached much sooner.

It had been suggested by N. Williams (see *Nature*, March 16, 1871), that the great brightness of the flame might be due to hydrocarbons; but analysis shows that this supposition is untenable. I think it more likely that the reason why we get such a bright flame from carbonic oxide during the blow is, that it is burning at the mouth of the converter at a much higher temperature than we get when we ignite a jet of the cold gas, for it is evident that the carbonic oxide formed in the metal bath must have even a higher temperature than the metal itself, and this is superadded to the temperature developed by the carbonic oxide burning in air. This is in accordance with the explanation given by H. St. Claire

Deville and Kirchôff, of the increase of luminosity of flames when burnt under great pressure; viz., that the temperature of the flame is thereby increased.

Alterations of temperature produce changes in spectra, and I think it will be found that this Bessemer spectrum, or at least that part of it which is due to carbon, is simply the spectrum of carbonic oxide of the particular temperature at which it is burning at the mouth of the vessel.

Spectrum Observations Show	Analysis of the Gas Shows
1st stage, 0′ to 4′ Faint continuous spectrum. No actual flame,	Carbonic acid evolved. but little or no carbonic oxide.
" 4′ to 8′ Sodium, potassium, and lithium lines appear. Towards the close, occasional flashes of carbon lines, ...	Carbonic acid still given off, with but little carbonic oxide. The temperature certainly rising, and causing the volatilization of alkaline metals.
2nd stage, 8′ to 10′ Dense flame, bright carbon lines in red, blue, and green fields, ...	Carbonic oxide evolved in quantity, and burning at a high temperature at the mouth of the convertor.
" 10′ to 14′ Bright green carbon lines, more distinct,	Carbonic oxide much increased in quantity.
" 14′ to end. Carbon lines bright till close, when they suddenly disappear,	Carbonic oxide still being evolved up to end of reaction.

It may be interesting to compare the composition of the gas, during the latter part of the blow, with other available gases met with in iron-works. I have selected as blast furnace gases a sample of gas from a Cleveland furnace, by I. L. Bell, and one from a Bessemer furnace, by William Crossley, and have added two samples of gas from Siemens' producer, at Dowlais, which I have had occasion to analyze—

TABLE VII.

	Siemens' Producer Gas.		Bessemer Convertor mean composition of gas during last half of blow.	Cleveland Blast Furnace Gas.	Askam Furnace on Bessemer Pig.
	No. 1.	No. 2.			
Carbonic acid, ...	4·3	5·2	1·34	17·30	8·36
Carbonic oxide,..	25·6	24·4	31·11	25·2	34·97
Hydrocarbons,...	2·8	traces.	—	—	—
Marsh gas,.....	1·6	2·4	—	—	—
Hydrogen,.....	—	8·6	2·00	·1	2·16
Nitrogen, &c.,...	65·7	59·4	65·55	57·4	54·51
	100·0	100·0	100·00	100·0	100·00

It will be seen from these analyses that the gas from the Bessemer convertor, during the last half of the blow, is really of as much value as any gas made purposely, or incidentally, at an iron-works. This is a most important fact; and if we consider the amount of fuel thus going to waste, the question naturally suggests itself whether it cannot be made available.

If we assume that, during the latter half of the blow, two-thirds of the total carbon in the pig is burnt, and take the melted iron to contain 3½ per cent. of carbon, we find that a Bessemer works, using only 1000 tons of such pig per week, is wasting a quantity of fuel equal to 23⅓ tons pure carbon, or say 25 tons coke.

Now, I would suggest that it is possible by simple arrangement to collect the gas and pass it under boilers, where it would save its equivalent of coal. The large body of flame is not wanted for any purpose. True, the workman now depends upon its indications to afford him the means of judging when the blow is completed; but the spectroscope would do this, with greater accuracy, with a fraction of the gas which now roars from the convertor.

The nature of the gases evolved during the blow will, of course, vary with the quality of the iron used; but as it is not possible to use iron with much less than 3 per cent. carbon, the quantity of carbonic oxide evolved cannot be much less than that found in the foregoing analysis; and I believe that whatever may be the nature of the iron, the general results would be the same.

Comparison of amounts of silicon and carbon oxidised—

TABLE VIII.

No. 1.	Silicon,	72·91	100·00
	Carbon,	27·09	
" 2.	Silicon,	69·80	100·00
	Carbon,	30·20	
" 3.	Silicon,	69·01	100·00
	Carbon,	30·99	
" 4.	Silicon,	39·58	100·00
	Carbon,	60·42	
" 5.	Silicon,	4·24	100·00
	Carbon,	95·76	
" 6.	Silicon,	3·34	100·00
	Carbon,	96·66	

Comparison of amounts of carbon oxidised to CO and CO_2—

TABLE IX.

No. 1.	C to CO,	—	100·00
	C to CO_2,	100·00	
" 2.	C to CO,	31·52	100·00
	C to CO_2,	68·48	
" 3.	C to CO,	35·54	100·00
	C to CO_2,	64·46	
" 4.	C to CO,	84·54	100·00
	C to CO_2,	15·46	
" 5.	C to CO,	92·72	100·00
	C to CO_2,	7·28	
" 6.	C to CO,	95·87	100·00
	C to CO_2,	4·13	

∴ C to CO_2 = 259·81
C to CO = 340·19

600·00

That is, $\frac{13}{30}$ths of the total carbon is oxidised to CO_2, and $\frac{17}{30}$ths to CO.

These results have since been corroborated by M. Adolf Tamm, in the *Jern Kontorets Annuler* for 1875, on "The Chemical Composition of the Gases emitted from the Bessemer Convertor during the Blow." The experiments were made at the Westanfors Bessemer Works, Sweden, the iron used being charcoal pig made at the same works, the analysis of which, and of the steel produced during the A series, were given as follows (Table XI.).

TABLE X.

TABULAR STATEMENT, SHOWING COMPOSITION OF GASES AND SPECTROSCOPIC OBSERVATIONS DURING THE BLOW.

	No. 1. 2 minutes from start.	No. 2. 4 minutes.	No. 3. 6 minutes.	No. 4. 10 minutes.	No. 5. 12 minutes.	No. 6. 14 minutes.
Carbonic acid,.....	10·71	8·57	8·2	3·58	2·3	1·34
Oxygen, ...	·92	—	absent.	none.	none.	none.
Carbonic oxide,.....	none.	3·95	4·52	19·59	29·3	31·11
Hydrogen, ...	—	·88	2·00	2·00 prob.	2·16	2·0 prob.
Nitrogen,.....	88·37	86·58	85·28	74·83	66·24	65·55
Hydrocarbons,.....	—	—	—	—	absent.	—
	100·00	100·00	100·00	100·00	100·00	100·00
Observations with spectroscope and naked eye,..	Faint continuous spectrum. No actual flame. Abundance of sparks thrown out.	Sodium line just appearing, but in flashes. Abundance of sparks.	Sodium, potassium, and lithium lines. Quantity of sparks decreasing.	Full spectrum, including the carbon lines. Flame dense and bright. Very few sparks.	Full spectrum. Dense flame. Still fewer sparks.	Full spectrum. Dense flame. Scarcely any sparks.

TABLE XI.

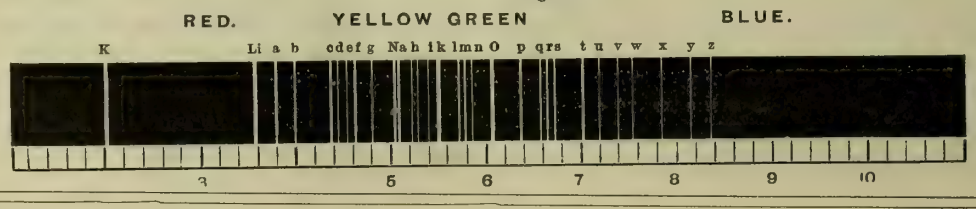
Series.	Minutes from commencement of blow.	Oxygen.	Carbonic Acid.	Carbonic Oxide.	Hydrogen	Nitrogen.
A,.....	3 to 5	4·762	9·127	—	—	86·111
A,.....	9 to 10	1·699	5·999	17·555	·908	73·840
A,.....	21 to 23	·967	4·856	19·322	1·120	73·735
A,.....	26 to 27	·550	1·853	14·311	1·699	81·587
B,.....	2 to 3	7·256	6·608	—	—	86·136
B,.....	8 to 10	1·296	5·613	15·579	1·112	76·400
B,.....	12 to 15	·980	4·144	25·580	1·040	68·256
B,.....	17 to 19	1·318	2·995	25·606	1·120	68·961

Solid Material Ejected from the Convertor.—In the early stages of the blow large quantities of sparks are emitted with the gases. The bulk of these come out as bright white specks, but quite a large number scintillate beautifully on leaving the vessel. These latter are due to particles of metal which are caught up as spray by the blast, but only burn when they reach the atmosphere outside. The remainder of the sparks are minute globules, which on analysis gave 52·82 per cent. iron, and 27·90 silica. They are very remarkable on close examination, consisting largely of spherical boom-shaped particles, or hollow spheres, with a small opening in each.

When manganiferous iron is being blown volumes of white smoke accompany the flame from an early stage, but with English pig iron this only makes its appearance towards the end of the blow. It consists of the oxide of manganese, which is carried out of the vessel with the blast. As soon as the carbon, silicon, and manganese have been all burnt out the iron begins to burn, and the colour of the smoke changes from a white or grey to ruddy-brown. This change is one of the best indications the blower can have when treating very siliceous pig iron. If iron of low grade be used, an extremely rapid evolution of gas takes place at a particular portion of the process, and large quantities of metal and slag are thrown out of the vessel. A similar eruption takes place even with iron of fair grade if it is allowed to get too cold before the blow is commenced; but with rich graphitic pig, highly siliceous iron, or metal containing from 2 to 4 per cent. manganese, the process goes on evenly and with little or no ejection of slag.

Spectrum of the Bessemer Flame.—The flame produced by the Bessemer process is so intense, that very early attempts were made to utilize the spectroscope in directing the operations. There is, however, so little difficulty in blowing English pig iron by the unaided eyesight, that the use of the spectroscope has not been followed up as it ought to have been. With the highly manganiferous pig iron often used on the Continent, there is difficulty in applying the spectroscope; but in special cases, and particularly when it is in constant use, it affords valuable indications of what changes are taking place. The general indications of the spectroscope have been mentioned above; but subsequently to writing the paper, SNELUS discovered that there exists some relation between the time of the first appearance of certain bright lines and the ultimate length of the blow. Thus, the two bright lines in the red portion of the spectrum marked *c* and *f* appear to come into full view when the mid point of the blow has been reached, if iron containing little manganese and about 2 per cent. silicon is used. These lines are believed to be due to carbon. Most of the lines in the green portion are due either to carbon or manganese, but the subject has not been studied sufficiently to account for all the lines. The spectrum is very brilliant and characteristic. The principal lines produced by English hematite are shown in the following diagram:—

Fig. 19.



These appeared in the following order in a "blow" lasting eighteen and a half minutes:—5·57, turned on blast; 6·1, Na; 6·4, Li; 6·5, *k*; 6·5½, K; 6·6, *c* and *f*; 6·6½, *t*; 6·7, K; 6·14¾, lines towards blue end gone; 6·15½, all lines gone except Na, Li, and *k*.

If the gas from the convertor be collected and burnt at a jet, we get the ordinary spectrum of carbonic oxide.

Generation of Heat by the Bessemer Process.—This subject has been investigated by Akerman, Jordan, Kupelwuser, and others. But in making the calculations it has been generally assumed that the carbon is entirely converted into carbonic oxide, whereas it will be seen, from the foregoing analyses, that $\frac{13}{30}$ of the total carbon is converted into carbonic acid, and only $\frac{17}{30}$ into carbonic oxide. This introduces a considerable error into previous estimates. There are also some factors that are necessary to an accurate result, which must be assumed for the present. Therefore, the following figures can only be approximate.

We will take the case of a Bessemer pig iron containing 2 per cent. silicon and 3·5 per cent. carbon, which is about the average composition of the molten iron run into an English convertor. A considerable portion of the iron itself is oxidised during the blow, possibly less than Akerman assumes; but for convenience we will accept his estimate of 6 per cent. There is a good deal of doubt about the calorific power of the iron so burnt; and as to the exact specific heats of some substances under consideration, probably the following figures will be sufficiently accurate:—

Calorific power of C burnt to	CO_2	=	8080
" C "	CO	=	2403
" Si "	SiO_2	=	7830
" Fe "	FeO	=	1201
Specific heats of	CO_2	=	·21
"	CO	=	·24
"	N	=	·24
"	O	=	·21
Molten iron		=	·16

We will also assume with Akerman that the temperature of the molten pig iron is 1400° C., and that the gaseous products leaving the convertor go off at 1400° C. (This latter figure must be below the actual).

Taking cwts. as the unit, 100 cwts. of iron contain 3·5 cwts. of carbon; $\frac{13}{30}$ of this, or 1·51 cwt., are burnt to CO_2, and $\frac{17}{30}$, or 1·98 cwt., to CO. ∴ Carbon burnt to CO_2, produces 8080 × 1·51 = 12,200 units of heat; but 1·51 cwt. C requires $\frac{1{\cdot}51 \times 16}{6}$, or 4·02 cwts. oxygen, and forms 1·51 + 4·02 = 5·53 CO_2. As the oxygen is obtained from the atmosphere, there will be $\frac{4{\cdot}02 \times 77}{23} = 13{\cdot}45$ cwts. nitrogen mixed with it. Now both the CO_2 and N leave the convertor in a gaseous state, and therefore they carry with them (5·53 × ·21 × 1400) + (13·45 × ·24 × 1400) = 6145 units of heat, leaving 12,200 − 6155 = 6055 units to increase the temperature of the bath. Similarly the carbon burnt to CO produces the following results:—2403 × 1·98 = 4757 units produced; but 1·98 C. requires $\frac{1{\cdot}98 \times 8}{6} = 2{\cdot}64$ cwts. O, and forms 4·62 CO_2. With the O there will be $\frac{2{\cdot}64 \times 77}{23} = 8{\cdot}83$ N, and the CO and N will carry away (4·62 × ·24 × 1400) + (8·83 × ·24 × 1400) = 4419 units, leaving 4757 − 4519 = 238 to add to the heat of the bath.

Again, 2 cwts. silicon burnt to SiO_2 produces 2 × 7830 = 15,660 units. Silica being a solid body, mostly remains in the vessel as slag. As it is impossible to ascertain with accuracy the difference between the specific heats of the silicon and silica, and of the iron and oxide of iron, it will probably be sufficient in each case to deduct the heat required to raise the oxygen consumed from 0° to the temperature of the bath.

Two parts silicon require $\frac{2 \times 16}{14} = 2{\cdot}28$ oxygen, and with this will be associated $\frac{2{\cdot}28 \times 77}{23} = 7{\cdot}63$ nitrogen; (2·28 × ·21 × 1400) + (7·62 × ·24 × 1400) = 3230 units have to be deducted from 15,660, leaving 12,430 for heating the bath.

Six cwts. Fe burnt to FeO, produce 6 × 1201 = 7206 units, and require $\frac{6 \times 8}{28} = 1{\cdot}71$ oxygen, with which then will be $\frac{1{\cdot}71 \times 77}{23} = 5{\cdot}72$ N. (1·71 × ·21 × 1400) + (5·72 × ·24 × 1400) = 2424. Therefore, from the iron burnt, there will be 7206 − 2424 = 4782 units for heating the bath.

Summing these results, we have for adding to the heat of the bath:—

From C converted to	CO_2,	.....	6055
" C "	CO	.....	238
" Si "	SiO_2,	.....	12,430
" Fe "	FeO,	.....	4782
			23,505

If there were no loss of heat by radiation and absorption by the sides of the convertor, the temperature of the bath would be (without taking into account the loss in weight of the metal) $\frac{23{,}505}{100 \times 16}$ = 1469° C. higher than at the commencement; so that the final temperature would be 1400 + 1469 = 2869° C. A considerable reduction must be made for the heat taken up by the lining of the vessel and for loss by radiation, but at present no exact figures for these can be given. It is probable that not more than three-fourths of the heat developed is really taken up by the metal, and thus the final temperature would be about 2000° C. This is the figure given by Akerman; but the amount of silicon has been taken at 2 per cent. instead of 1 per cent., which he assumes for Swedish iron, while the heat developed by the combustion of carbon is really greater than he makes it. It will be seen, however, that more than half the heat developed is due to the silicon. This agrees with practical experience. It will also be evident, that since the

bulk of the silicon is oxidised early in the blow, during which period also the carbon is burning to CO_2, the rise in temperature must be proportionately greater during this period than during the latter half. This also accords with spectroscopic observations; for the changes in the flame are remarkably rapid till towards the middle of the blow, after which the heat does not appear to increase greatly. If the blast be continued after the whole of the carbon, silicon, and manganese have been burnt out, the iron is burnt very rapidly, and peroxide of iron is formed, which is carried out of the vessel in dense volumes of brown smoke. This carries off so much heat that, instead of the temperature of the remaining metal rising, it is rapidly decreased, and overblown metal is rarely fluid enough to allow of its being cast without skulling in the ladle. On the addition of spiegeleisen to such overblown metal, the combustion of its carbon, manganese, and silicon, by the dissolved oxide of iron, takes place with explosive violence.

We have no means of measuring the final temperature of the metal with accuracy, but we know that it is above the melting point of platinum, which Deville places at about 1900° C. A stream of the molten steel will rapidly fuse wrought iron, and when the pig contains 2 per cent. or more silicon, the steel will remain fluid in the ladle for a considerable time; thus showing that the final temperature is much above the melting point of steel. In the foregoing remarks no mention was made of manganese, English pig iron rarely containing any quantity. But on the Continent iron containing up to 4 per cent. manganese is constantly used; and from the fluidity of the steel produced, it appears that the combustion of this manganese adds considerably to the heat of the bath. But as the calorific power of manganese is not known, it is needless to consider the subject further.

Fig. 20.

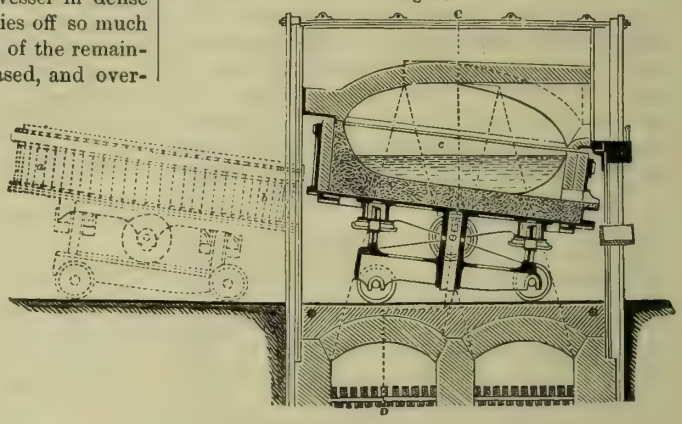
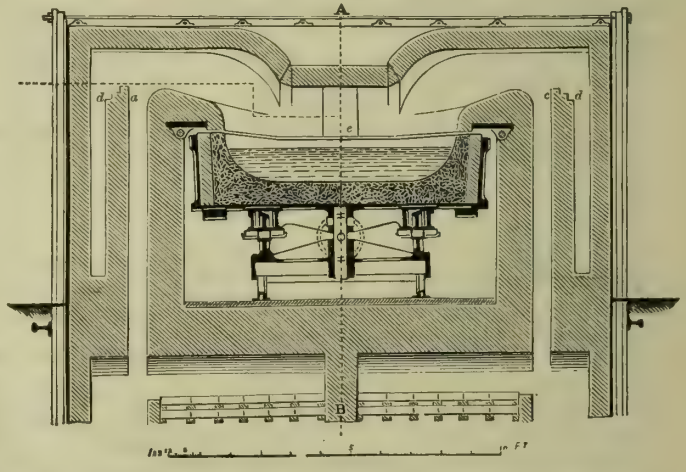


Fig. 21.



Open-hearth Process of Steel-making.—Heath patented the manufacture of steel by melting scrap iron or its equivalent in a bath of pig iron in a reverberatory furnace heated by gas, so long ago as 1845; but no really successful results were attained, owing to the impossibility of producing a sufficiently high and equable temperature, until Dr. Siemens perfected his regenerative gas furnace. The applicability of this furnace for steel-melting was patent to all; and Messrs. Siemens refer to this use of their system in their patent of 1861. In England, however, Attwood was the first to practically use the furnace for steel-making, while W. M. Martin in France carried success to a higher point, by using a mixture of pig iron, iron scrap, and iron ore. In 1867 Siemens took up the question himself, and erected an experimental furnace at Birmingham. He patented his plan of steel-making, and in a short time succeeded in placing the manufacture on a permanent footing. Shortly after the Landore Siemens Steel Company was started, and four 5-ton furnaces were erected for carrying on the process on a commercial scale. The absolute necessity of the Siemens regenerative principle to any open hearth system of steel-making, has led to the general application of the terms "Siemens" or "Siemens-Martin" steel to all steel made by open-hearth processes.

In 1876 Pernot introduced a modification of the Siemens furnace, in which the bed of the furnace is made circular, and so arranged that it can be rotated on an axis which is inclined 5° or 6° from the vertical. Thus, the bed dips to one side, and while the fluid metal lies on this side any solid portions are carried round, exposed to the full heat of the flame, and then dipped at each revolution into the bath. By this means more rapid oxidation takes place than with the fixed furnace.

The general arrangements of the Siemens steel-

melting furnace are described under the article Fuel. In the drawings of the Pernot furnace (Figs. 20, 21) *a*, *b* is the furnace bed, which is fixed on an inclined pivot, and revolves on rollers by means of gearing—it can be drawn out from under the roof for repairs; *c*, *d* are the gas and air ports; *e*, *e* is the bath of metal. At St. Chamond there are now one 10-ton, one 15-ton, one 20-ton Pernot furnaces at work, and three more 20-ton furnaces are being erected.

The gas is made in producers, which are thoroughly described in the article on Fuel. It consists mainly of carbonic oxide and nitrogen, as will be seen from the following analyses.

	No. 1.		No. 2.
Carbonic acid,	4·3	....	5·2
Carbonic oxide,	25·6	....	24·4
Hydrocarbons,	2·8	....	traces.
Marsh gas,	1·6	....	2·4
Hydrogen,	—	....	8·6
Nitrogen,	65·7	....	59·4
	100·0		100·0

Sample No. 1 was made with the ordinary producer, with natural draught; No. 2, with a closed ash-pit and artificial blast induced by a jet of steam. Hence the rather large quantity of hydrogen. This gas is conveyed in wrought-iron tubes or in underground culverts to the furnace, the producers usually being at some distance off. In the modifications of gas furnaces known as the Bischeroux and Ponsard, the producers are placed close to the furnace. This saves coal, but is not so convenient as Siemens' plans.

The melting furnace is a rectangular structure, cased with wrought or cast plates, and firmly braced together by a system of girders, which require to be very carefully tied above and below the furnace; old bridge rails are often used for the girders, but at Creuzot regular bridge girders are employed, as they have to resist a great strain to prevent the expansion of the roof from pushing out the sides of the furnace. The side walls of the furnace are built of the best firebricks; those made at Glenboig in Scotland being particularly suited to this portion of the work and for the regenerators, on account of their being hard, strong, and withstanding great heat without changing form. The roof of the furnace is built with silica or ganister bricks, as no others will stand the intense heat of this part of the structure. The bed of the furnace is supported, so as to leave a clear space underneath it and around the gas ports, in order that these parts may be cooled down by a free circulation of air. The hearth is thickly lined with pure quartzose sand, which is soon consolidated by the intense heat. It is shaped into a shallow dish-like form to hold the metal, which is tapped out through a hole in the middle of the side plates. The tap-hole is stopped with a little coke dust, and then sand and coke dust outside. This is easily removed when the metal is to be tapped; while if sand alone be used, it becomes hardened to such an extent, that there is often great difficulty in opening the tap-hole. Below the furnace proper, and sunk in the ground, are four regenerators. These consist of brick chambers, which are loosely filled with firebricks, and communicate by passages above with the furnace, and below with the gas and chimney flues, by means of reversing valves, so that two of the chambers can be alternately connected, either with the gas flue or chimney flue, and two with the external atmosphere and with the chimney flue. The passages above open into the furnace by "gas" and "air ports," which are narrow passages about 5 inches wide. The air ports are made to open into the furnace above the gas ports, for the purpose of getting a thorough mixture of gas and air. The roof of the furnace dips from each end towards the centre, at an angle of about 30° with the horizontal, so as to deflect the flame on to the metal. After combustion in the furnace, the products are drawn down by the chimney through a pair of the regenerators, and in passing over the large surface of brickwork the greater part of the heat is abstracted, to be restored to the incoming gas and air, which are made to pass through these chambers, and out by the remaining pair when the current is reversed by altering the valves. This is done about every half hour.

The subsidiary apparatus for steel-making by this process is in many respects similar to that described for the Bessemer process; but in most of the steel works arranged by Siemens the furnaces are placed in a line, and the casting pit runs in front of them, sometimes, as at Landore and Panteg, between two sets, and is served by an overhead travelling crane for the removal of moulds, ingots, &c. At Dowlais, and at Messrs. Spencer's on the Tyne, hydraulic casting and ingot cranes are used. At Terre Noire a circular casting-table, moved from below by rack and pinion, brings each mould alternately opposite the tap hole, thus avoiding the use of an intermediate ladle. At Creuzot and at Bolton somewhat similar plans have been employed; but on the whole the hydraulic arrangements of Bessemer, though most costly, are best suited for this work.

Methods of Conducting the Process.—There are two distinct plans of working—the first may be called the "scrap" process, the second the "ore" process. In either case a bath of pig iron is the starting point. In the scrap process this may be very small, say from 6 to 10 cwts. for a 5-ton charge. The pig iron is usually melted in the furnace itself, as is also the other material employed; but at Terre Noire, and most continental works, a small "dandy" furnace is placed by the side of the larger furnace for the preliminary heating of the material. This is a very useful adjunct, and facilitates the process materially, while at the same time it saves wear and tear of the large furnace. Having got the bath of pig iron, small charges of scrap of all kinds are placed on the sloping bank, and as they get heated are pushed down into the metal bath; fresh charges being added as fast as dissolved. In this way, after the lapse of eight to ten hours, a bath of 5 to 10 tons of metal is obtained, which is practically pure iron, if iron free from sulphur and phosphorus has

been used, since all the carbon, silicon, and manganese are rapidly burnt out of the pig iron. As in the Bessemer process, however, the metal at this stage will not work, being highly red short. In order to produce a malleable product ferro-manganese is added if very soft steel be required; spiegeleisen, if such as rail or tool steel is wanted; and a mixture of ferro-manganese and siliceous pig iron (or a special alloy containing silicon and manganese, which may be termed mangan-siliconeisen), when steel castings are to be made. With 6-ton charges from 70 to 100 tons of ingots per week can be made from one furnace.

In the "ore" process the charge is nearly all made of pig iron. About 5 tons of No. 3 hematite are melted down, and about 1 ton of iron ore, free from phosphorus and sulphur, broken to the size of hen eggs, is added to the charge in small quantities at a time, keeping up a regular boil, until all the carbon, silicon, and manganese have been removed by the reaction between the oxygen of the ore and these constituents of the pig iron. As in the previous case, small samples are taken from the bath from time to time and tested by the hammer and an examination of the fracture, until the metal is found to be malleable, and the fracture shows a lead-like crystallization. The spiegel or ferro-manganese is then added, and the metal tapped out rapidly to prevent waste of these latter substances. From 20 to 25 cwts. of ore are required for a 5-ton charge, and, according to Hackney, "of the metal contained in the ore about one-half passes into the steel, so that, as the carbon and silicon in the pig amounts to about 8 per cent., the yield of ingots and scrap is generally 1 to 2 per cent. more than the weight of pig iron and spiegeleisen put in. The consumption of coal is slightly larger than in the scrap process, as there is more slag on the surface of the metal, and hence the flame must be maintained at a higher heat. The wear of the furnace roofs is also somewhat greater than in working scrap, and for the same reason, the more intense heat of the flame; and in addition to this, the splashing of the slag in the ore process helps to wear away the roof. A careless furnaceman, with plenty of heating power at command, may bring the furnace roof down in a day; but in practice and with reasonable care, a roof of good bricks will last, even in working pig iron, from one hundred to two hundred charges. The two methods of working above described are often combined; that is, if there is a limited quantity of scrap to be worked, it is divided among the furnaces, and the charges are finished by adding ore."

Speaking of the Pernot furnace Hackney says:—"The working of the Pernot furnace at Saint Chamond and Allevard differs in many points from that of the fixed furnace. In melting together pig iron and scrap, the former, previously heated to redness in an auxiliary furnace, is spread uniformly over the bottom, and upon this the whole quantity of steel rail ends, or other scrap employed, is charged at once, and the furnace is left to itself. As the bed keeps constantly moving round, each piece of scrap is alternately exposed to the full heat of the flame, and dipped into the bath of melted metal that soon begins to form. The fusion is thus very rapid; the whole mass is liquid within two hours; samples are then taken out at intervals, and when the metal is sufficiently soft, spiegel is added, and the charge is tapped. Five charges of about 4½ tons each are got out in each twenty-four hours. The proportion of materials in the total charge is—pig iron, about 24 per cent.; steel scrap, 67 per cent.; and spiegel, 9 per cent. The loss is between 6 and 7 per cent., and the coal used per ton of steel made is 8 to 8½ cwts. Comparing with this the average working during two months of furnaces of the same design, but with fixed beds, at Terre Noire, about the same proportions of materials are used, and the waste is the same; but the output, instead of being nearly 11 tons per twelve hours, is little more than 5½ tons, and the coal used per ton of steel is nearly 18 cwts."

The following table, by A. Willis of Landore, exhibits the rates of oxidation of carbon, silicon, and manganese in the open-hearth process:—

Samples Taken.	Contained—		
	Carbon.	Silicon.	Manganese.
	Per Cent.	Per Cent.	Per Cent.
When pig was melted,...	1·90	·570	1·140
One hour later,.....	1·80	·233	·576
Two hours later,.....	1·70	·183	·200
Three "	1·65	·050	·080
Four "	1·60	Manganese and silicon completely gone.	
Five "	1·10		
Six "	·60		
Seven "	·20		

It is evident from the above that a considerable amount of oxidation must have gone on during the process of melting down, as is the case in melting pig for puddling, since the iron would have contained more than 1·9 carbon and 0·57 silicon. This is to be expected, and it is on this account that there is not the same advantage in starting with molten pig iron direct from the blast furnace as there is in the Bessemer process; for oxidation goes on more rapidly during the time the pig is being melted down than when it is all fluid, owing to the much greater surface exposed by the lumps of pig iron than by the fluid metal.

Many attempts have been made to obtain iron direct from the ore as iron sponge, and to melt this down to form steel. Chenot, in France, carried on the direct reduction for a considerable time, and met with a fair amount of success, but failed on account of the difficulty in securing perfect reduction. Blair has carried the direct reduction a step farther, and has succeeded in making a considerable quantity of steel by melting the sponge (produced as described in the article on Iron) in an open-hearth furnace at Pittsburg; but so far the plan has not been commercially successful.

Siemens has attacked the problem in a different way, and has taken out a series of patents for what he terms "The direct process." The production of iron by this plan was described also in the article on Iron, and it is only necessary to treat the

metal so made as in the scrap process to produce steel; but so far this, also, has not yet been commercially successful—possibly because at Towcester, where the process was carried on, there was no melting furnace to make the directly-reduced iron into steel at once, and as a process of *iron* making it did not pay.

Physical Properties of Combinations of Iron with other Elements.—There is little doubt that a large number of elements may and do unite with iron, but only the action of the following need be considered here:—viz., carbon, silicon, sulphur, phosphorus, manganese, oxygen, copper, tungsten, and chromium. It is rarely that the opportunity is afforded for studying the action of these substances upon iron singly. An attempt to do so was made some years ago by the British Association; but no results of any importance were obtained. We have, therefore, to make deductions from a study of the qualities of various combinations as they arise.

Carbon is generally considered to be the essential *steel*-forming element. If iron be nearly free from other elements, the presence of ·1 per cent. carbon, or even ·15 per cent., produces scarcely any hardening effect upon the alloy, as such a compound may be plunged while red hot into cold water and remain perfectly soft and ductile. As the proportion of carbon increases, the hardening effect of such treatment becomes more and more evident, until, with anything approaching 1 per cent. of carbon, the steel becomes very hard and brittle by sudden cooling. Even when containing about 2 per cent. carbon it does not quite cease to be malleable; but it requires great care in the heating to prevent the carbon being burnt out, and can only be forged at a moderate red heat. If small quantities of silicon, phosphorus, or manganese be present, it is not possible to work steel containing even this small quantity of carbon. Manganese appears to favour the solution of carbon in pig iron, since an alloy containing 8·55 manganese contained also 6·62 of carbon, and the carbon appears to rise with the manganese.

The action of carbon upon iron is very remarkable; and though the effects are tolerably known, the cause of its action is even yet shrouded in mystery. Thus it is well known that when anything like 1 per cent. of carbon is present, the alloy suffers remarkable changes from various modes of treatment. If it be heated and plunged into a fluid that abstracts heat rapidly, it becomes hardened in proportion to the rapidity of this action, and thus under the same conditions mercury causes greater hardness than water, and water than oil. When a piece of steel has been hardened and is again heated, the hardness disappears as the temperature is raised. Thus if a certain degree of hardness is required, it may either be obtained by first pushing it to the extreme point, as by raising the steel to a dull red heat and plunging in water or mercury, and afterwards gradually raising the temperature of the metal to a certain point and leaving it to cool of itself; or else the piece may be raised to a definite temperature, and then suddenly cooled in a vehicle that only abstracts the heat slowly, as oil. According to the experiments at Terre-Noire, it appears that tempering steel (whether containing much or little carbon or manganese) in oil about doubles the tensile strain, while the elongation is reduced in the same or even greater degree. The process of producing a certain degree of hardness is termed "tempering," and is quite an art. In raising the steel to the required temperature the workman is aided by the colour produced upon the surface of bright steel by slight oxidation, as the thin film of oxide passes through a regular series of colours, from light straw to brown, then blue, and finally black, through every gradation in shade. Thus it is that the "temper," as the degree of hardness is called, is determined by this colour. The following table (XII.) shows the colours produced in tempering carbon steel for particular uses:—

TABLE XII.

Temp. F.	Colour.	Temper.
430	Very faint yellow.	Lancets.
450	Pale straw.	Razors & surgical instruments.
470	Full yellow.	Penknives.
490	Brown.	Scissors and cold chisels.
510	Brown, with purple spots.	Axes, plane irons, pocket knives.
530	Purple.	Table knives, large shears.
550	Bright blue.	Swords, watch springs.
560	Full blue.	Fine saws, augurs.
600	Dark blue.	Hand and pit saws.

The process of tempering should leave the steel of the hardness required, with the minimum of brittleness. Tempering in oil appears to produce this result best.

No perfectly satisfactory explanation of the theory of hardening and tempering has yet been adduced. One set of metallurgists suppose that steel contains a certain quantity of graphite, or uncombined carbon, and that when the steel is heated this enters into combination with the iron, and that sudden cooling keeps it combined.

Probably a more satisfactory explanation is that when the steel is heated it is expanded and its particles put into a state of tension, which is retained by instantaneous cooling. Chemical analysis has not satisfactorily proved that tempered steel contains more combined carbon than untempered steel, while it is well known that tempered steel has a less specific gravity than untempered steel, and that the process of hardening increases the size of the article slightly. Thus the specific gravity of cast steel at 11° C. was—Unhardened, 7·9288; hardened, 7·6578; and a bar of steel which before hard ning had a volume of 20 c.c., became 20·351 after hardening. The expansion by hardening can be easily proved by rivetting together a piece of soft iron and a piece of steel, carefully filing the edges true. On heating and hardening this compound plate, the edges of the steel plate will be found to overlap those of the iron, while the rivets will probably have been sheared. Hardened steel is much less readily acted upon by acids than the same steel in a soft state, and the

action of the acid produces a different effect in the the two cases.

Steel for ship plates and angles should not contain much above ·1 per cent. carbon. If such metal is also free (to about the same extent) from silicon and phosphorus, it not only does not harden, even though it may contain nearly a half per cent. of manganese, but is rendered tougher by repeatedly heating and plunging into cold water. It can also be welded with facility, although it requires more care than iron. Such metal will possess a tensile strength of from 25 to 28 tons per square inch, and will elongate from 25 to 30 per cent. in a length of 8 inches before rupture. For boilers the steel may contain up to ·25 per cent. carbon without becoming too hard. The extra carbon adds considerable strength and stiffness to the material, while it tends to prevent oxidation. It does not weld quite as easy as the softer kind, but still may be welded perfectly. It hardens very slightly, and in the soft state possesses a tensile strain from 28 to 34 tons to the inch, with an elongation of 20 to 25 per cent. For rail steel the carbon may range from ·25 to ·5 per cent., and the tensile strain will run up to about 45 tons to the inch, and the elongation over the 8 inches decrease to about 10 per cent. Tool and cutlery steel may contain from $\frac{3}{4}$ to $1\frac{1}{2}$ per cent. carbon, and the tensile strength will increase up to about 70 tons to the inch, the elongation decreasing from 5 to 1 per cent. By particular modes of tempering, such hard steel, when free from other elements, may be strengthened until, in the state of wire, it will stand a strain of over 100 tons to the square inch.

Carbon steel becomes hardened by cold rolling or hammering. The appearance of the fracture is a good guide to the quantity of carbon present in a steel free from other elements. With from one to two tenths per cent. the fracture will be silky and almost fibrous, with ·5 per cent. it becomes coarsely granular, while with 1 per cent. the grain becomes very fine and silvery.

Carbon tends to prevent red shortness; but as the fusing point is rapidly lowered by an increase in the percentage of carbon, it is important to work the more highly carburized materials at a heat not above blood red, while the softer varieties may be worked at a white heat.

Silicon produces both red shortness and cold shortness in steel. In the absence of carbon these effects are not very marked, but when very small proportions of carbon are present the action of silicon is very decided. Thus, when the carbon is under ·1 per cent., silicon may exist up to ·6 per cent., or more, without rendering the steel particularly brittle. Such steel could be heated and quenched in water, and afterwards bent double without cracking, while the tensile strength was not greatly increased. It also worked well at a bright red heat. On the other hand, when the carbon rises to ·4 or ·5 per cent., even ·2 per cent. silicon produces decided red shortness and cold shortness, and if the silicon reaches one-half per cent. these qualities are developed to a dangerous extent. Where steel is not to be worked, however, as in castings, the presence of silicon is very valuable, as silicon steel runs solid and sets free from honeycomb, while after annealing it possesses considerable strength. In the following table, No. XIII., there is a case of a steel containing 2·44 per cent. silicon and ·40 per cent. carbon:—

TABLE XIII.—ANALYSIS OF STEEL OF VARIOUS QUALITIES.

	Very good Steel for Roll Turning. Crucible Manufacture.	Silicon Steel. Very fine grain. Tensile strain, 48 tons. Elongation, 3 per cent.	Ordinary Steel made by Siemens process at West Cumberland Iron and Steel Co.'s Works. Rolled well, and was very suitable for rails.	Crucible Steel for Punches—stood well.	Punch Steel, too hard to temper, cracked in hardening	Crucible Tool Steel, remarkable for its turning properties.	Steel Rail, worked remarkably well—W. Cumberland Iron and Steel Co.—but the least red-short.	Steel Plate which would not take a good edge—West Cumberland Iron and Steel Co.	Bessemer Steel Punch made at W. C. I. & S. Co.'s Works—worked 3 weeks without re-setting, & punched 1500 rails, or 6000 holes, only once tempered.	Red-short Steel, owing to excess of sulphur.	Terre Noir Steel. Made in Siemens furnace from old iron rails and scrap.
Iron,	97·803	96·140	98·558	98·696	98·737	98·000	98·656	98·784	98·586	99·180	98·820
Carbon,	2·000	·400	·370	·940	·820	1·850	·480	under ·100	·350	·340	·230
Silicon,	·093	2·440	·011	·130	·112	·144	·018	·833	·335	trace.	·102
Sulphur,	·014	·060	·030	·008	·006	·029	·022	·043	·038	·160	·063
Phosphorus,	trace.	·026	·057	·026	·095	trace.	·061	·075	·073	·060	·130
Manganese,	trace.	·880	·974	·200	·230	·230	·763	·216	·691	·360	·662
Total,	100·000	100 000	100·000	100·000	100·000	100·253	100·000	99·951	100·073	100·000	100·007

ANALYSIS OF STEEL OF VARIOUS QUALITIES.—*Continued.*

	Terre Noir Cast Steel. Very solid, without blow holes.	Creusot Gun Steel.	Crewe Steel Plate.	Red-short Steel. Red-short from excess of sulphur.	Red-short Steel. Red-short from overblowing.	Steel for Boiler Plates.	Plate Steel for Boilers and Ships. Test—stood 34 tons tensile strain per square inch. Elongated 20 per cent.	Test—27 tons tensile strain. Elongated 27 per cent.	Test—28 tons tensile strain. Elongated 25 per cent.	Test—31 tons tensile strain. Elongated 20 per cent.	Tool Steel. Crucible Manufacture.	Steel for Castings, made with Silicon Pig.	Steel for Castings—very sound & quite free from blowholes, & exceedingly hard—Turned Steel which Mushet's Steel would not touch.
Iron,	98·241	99·003	99·411	99·207	99 376	99·679	98·779	—	—	—	98·379	97·900	97·250
Carbon,	·450	·405	·260	·250	·200	—	·400	none.	·090	·140	1·280	·420	·500
Silicon,	·384	·010	·052	—	·056	—	·102	·018	·005	·028	·112	·521	·251
Sulphur,	·063	·010	·024	·133	·011	040	·019	—	—	—	trace.	·050	·085
Phosphorus,	·085	·025	·029	·05	·044	·022	·081	·031	·056	·026	028	·058	·043
Manganese,	·777	·180	·244	·360	·313	·259	·616	·273	·259	·259	·201	1·051	1·380
Total,	100 000	99·633	100 000	100·000	100·000	100·000	100·000	—	--	—	100·000	100·000	99·509

This steel could be heated and rolled, and was very fine in the grain. The tensile strain of the rolled bar was 48 tons per square inch, but it only showed 3 per cent. elongation. Steel containing much silicon will not take a coating of tin. An analysis of a sample of steel containing ·833 per cent. silicon, and very little carbon or manganese, is given in the table. It was found to be impossible to clean the surface of this steel so as to enable it to take a regular coating of tin. Sulphuric acid of various strengths, sulphate of copper, and chloride of zinc were tried for cleaning the surface; but in all cases the tin only adhered in patches, while there appeared to be a film on the surface of the metal, which was doubtless silica, and this in all probability prevented the tin getting to the clean metallic surface. The presence of silicon in rail steel may be detected during the process of rolling; as if there is even a very small quantity of silicon present, the fine scale produced in the finishing rolls adheres to the rail, or falls off in flat dry flakes, while if the steel contains only a trace of silicon this oxide leaves the steel freely, and falls off in curly scales. It is very probable that silicon may tend to prevent the oxidation of steel by forming an insoluble coating on its surface, in the same way that oxide of zinc and carbonate of lead protect the surfaces of zinc and lead respectively from further oxidation.

The presence of an excess of silicon in steel may also be detected by an examination of the fracture, which gradually becomes of a light chalky colour and fine grain as the silicon increases. Silicon is often left in the metal when all the carbon has been burnt out, both by the Bessemer and Siemens process, if the pig iron contains an excess to start with. Thus it is important to keep the silicon in pig iron down to about 2½ per cent. in pig iron to be melted in the cupola for the Bessemer process; and if taken fluid from the blast-furnace, even this quantity is too great, while the iron will blow sufficiently hot in the latter case if it contains no more than 1¼ per cent. It is pretty well proved that as carbon and manganese increase silicon decreases in pig iron.

Sulphur.—This element is extremely deleterious in steel that has to be worked, as the most minute proportions cause decided red shortness. One-tenth of 1 per cent. is so active that it is very difficult to get the steel containing that quantity to roll soundly. It does not appear to be of so serious consequence in tool and cutlery steel, as it does not produce brittleness. It is very objectionable in steel for castings, as it conduces to unsoundness in the metal. Its effect on the strength of steel has not been well made out.

Phosphorus is as active in producing cold shortness in steel as sulphur is in causing red shortness, and to about the same degree, while to a certain extent one element appears to counteract the other. Phosphorus is much more active in producing hardness in steel than carbon is; 1 part of phosphorus produces about the same absolute hardness that is caused by 2 or 3 parts of carbon. Still, if carbon be nearly absent, it is possible to have about ·25 per cent. of phosphorus present in steel intended for rails without its being unduly brittle, and even in plates a certain quantity is admissible provided carbon be nearly absent. When carbon is present to the extent of ·3 to ·5 per cent., ·1 per cent. phosphorus produces very decided brittleness. Steel for tools and cutlery should be very free from phosphorus, as it is not only extremely difficult to temper phosphorus steel (as may be seen from the tabulated analysis of steel punch), but for fine cutlery it is impossible to have a keen cutting edge with steel that contains much over ·025 per cent. phosphorus. On the other hand, there is no objection to a small quantity of phosphorus in steel for castings, as it tends to cause the metal to run solid without greatly reducing its strength.

Mr. Holley has recently made a careful set of experiments on the phosphoric steel introduced at Terre Noire, following the material all through the process of its manufacture. The following table shows the composition of the steels, and how they rolled, &c. Professor Thurston carefully tested all these steels mechanically, and the following are some of his notes:—"They are not as ductile as common steels. Their higher elastic limit is accompanied by a lower degree of toughness. They are harder, and rather less tough than the standard steels. Comparing these steels with common steels of similar temper, it would seem that these steels excel usually in strength, and in some cases are greatly superior in tenacity to ordinary steels. When exposed to sudden and excessive shocks they are more liable to break. The fractures are peculiar in appearance." (See Table XIV.)

Manganese is the most useful metal we have as an alloy of iron. While it adds slightly to the hardness of steel, especially when carbon and silicon are present, it does not induce brittleness unless other hardening elements are present. Even with 1 per cent. manganese steel may be very tough. But the great value of manganese arises from its tendency to neutralize red shortness. Where this is due to the use of excess of oxygen, the action of manganese is undoubtedly to remove it, owing to its greater affinity for oxygen. The oxide of manganese formed tends to the production of a very fluid slag, which promotes the soundness of the steel. In the case of red shortness due to sulphur it is doubtful whether the manganese actually removes, or neutralizes, the effect of the sulphur, or whether it acts only by removing the red shortness due to oxygen. It appears that, in addition to removing or neutralizing the red shortness, an alloy of iron and manganese up to 1½ per cent. of the latter actually works better than steel, in other respects similar, would do with the manganese absent. It was formerly the practice to add only sufficient spiegel to leave about ·25 per cent. manganese in the steel for rails, but in England steel makers find that by using richer spiegel, and more of it, so as to leave about 1 per cent. manganese in the steel, they can use rather lower and therefore cheaper grades of iron; the excess of

TABLE XIV.

COMPOSITION AND PROPERTIES OF PHOSPHORIC STEELS.

No. of Charge.	596.	598.	600.	601.	602.	603.	604.	611.	612.	634.	635.	636.	637.
Carbon,	0·230	0·220	0·193	0·220	0·172	0·230	0·450	0·121	0·123	0·110	0·124	0·103	0·430
Silicon,	·043	·034	·038	·046	·030	·042	·040	·013	·004	·056	·005	·017	·023
Sulphur,	·178	·109	·103	·099	·114	·080	·080	·054	·087	·078	·095	·089	·053
Phosphorus,	·383	·341	·334	·332	·360	·297	·288	·241	·299	·271	·254	·293	·255
Manganese,	·596	·484	·431	·689	·957	·672	·630	·390	·370	·502	·627	·562	·693
Result on rolling ingots,	Went to pieces in rolls.	Cracked badly.	Cracked badly.	Slightly better.	Still cracked, but better.	Much like 602.	Hard steel, cracked badly.	Worked fairly well. Steel was made at high temperature.		Made fairly merchantable bars, but not quite perfect.		Cracked rather badly, but fairly merchantable.	Cracked badly.
Order of merit as to malleability,	10	9	5	7	3	4		6	6	2	1	8	
Strength per square inch in lbs.,	37,500	35,500	37,000	42,000	37,500	36,000	35,000	33,000	34,500	36,500	33,000	35,000	48,250
Extension in 6-inch samples	Inches. ·3208	·3088	·3511	·3870	·3880	·2464	·0588	·5940	·6384	1·2884	·4551	·8134	·4530
Weight in lbs. to produce 1 inch compression in samples 5 inches diameter and 2 inches long,	487,804	448,430	819,672	952,380	697,628	438,596	724,637	418,410	497,512	537,634	699,300	444,444	862,069
Ultimate strength in compression of similar samples,	27,000	28,000	27,500	26,500	25,500	27,500	31,000	36,000	31,000	33,000	30,000	40,000	29,000

manganese neutralizing the increased quantity of sulphur in the lower grade of pig. An alloy of manganese and silicon with iron is exceedingly useful for the production of solid steel castings, and some excellent results have been obtained with it at Terre Noire, where this alloy was first introduced. An analysis of a fine sample of this mangan-silicon-eisen, exhibited by the Terre Noire Company in the Paris Exhibition, will be found in Table XIVA. Also an analysis of very rich ferro-manganese. This rich alloy of iron and manganese is now a regular blast-furnace product, and is very largely used for making soft steel. The oxides of manganese and iron unite readily with silica to form a very fusible slag, and thus they are removed from the metal, and leave it to run perfectly sound. Silicon steel shows no tendency to rise in moulds or emit gas; but it is only suitable for castings, as the silicon would render it difficult to forge.

Oxygen.—Overblown Bessemer metal is known to be particularly spongy and full of honeycomb, and there appears to be every reason to believe that nearly pure molten iron occludes oxygen and carbonic oxide in the same way that molten silver does oxygen; and that while the carbonic oxide is to a large extent ejected during the solidification of the metal, causing it to boil in the mould, only a certain portion of the oxygen escapes in this way, the remainder becoming sealed up in the metal. This portion probably gradually unites with the iron to form oxide, which is disseminated in infinitely small portions through the metal, but is sufficient to cause a break of continuity of its particles, so that when it is heated and forged, it can no longer hold together, but is highly red-short. The portion of oxygen that escapes from the metal during solidification oxidises a portion of iron at the surface, and gives rise to an abundance of sparks, the metal being what is termed "fiery." It is probable that the tendency of iron to occlude gases is increased by the presence of sulphur, and diminished by the presence of manganese, since we know that steel containing sulphur will not cast soundly, while mild steel made with ferro-manganese in the open-hearth furnace remains "dead melted," as it is termed. Snelus, by calculation from the quantity of carbon and manganese left in the metal, after adding a known weight of solid spiegeleisen of known composition to a certain quantity of Bessemer metal containing 1 per cent. carbon, found ·278 per cent. oxygen left in the metal; and Bender, by direct combustion of the steel in a current of hydrogen, and collecting the water given off, found ·35 per cent. oxygen in Bessemer metal containing ·08 per cent. carbon. Sergius Kern, by the same process, found in two samples of blown metal before spiegel was added, ·185 and ·171 per cent. oxygen; and after these samples had been heated, he found ·165 and ·162 per cent. respectively. It is quite possible that metallic iron may dissolve oxide of iron directly, in the same way that metallic copper dissolves oxide of copper. There are many very interesting points in connection with this portion of the subject, that

require close study and much further investigation in order to clear up the mystery that surrounds them.

Copper.—Small quantities of copper are occasionally found in steel, generally derived from the spiegeleisen. Some steel made at Harrisburg from pig iron, smelted from ore containing a considerable quantity of copper pyrites, was found to have as much as ·5 per cent. of copper, and yet is stated to have rolled well; but the general opinion of metallurgists is that copper induces red shortness in steel in about the same proportion as sulphur does.

Tungsten alloys with iron much in the same way that manganese does. The properties of this alloy have been successfully studied by Mushet, who has succeeded in introducing it commercially under the name of Mushet's "special steel." The analysis of special steel in Table XIVA is by Pattinson and Stead.

TABLE XIVA.

	Ferro Manganese.	Mangan Silicon Risen.	Special Steel.
Iron,	8·25	66·75	87·00
Combined carbon,	6·62	2·65	·62
Silicon,	0·093	10·20	·21
Sulphur,	trace.	trace.	03
Phosphorus,	0·145	0·185	·10
Manganese,	85·50	20·50	·73
Titanium,	—	—	nil.
Tungsten,	—	—	11·40
	100·608	100·285	100·09

Heeren found 8·73 per cent. and Willis 12·75 per cent. tungsten in other samples. It is extremely hard, breaking with a conchoidal fracture like that of hardened steel, and has a very fine grain. It can only be forged at a moderate heat, and absorbs heat much more slowly than ordinary steel, so that it should be raised in temperature very gradually. It is so hard that it needs no tempering, and thus tools for turning and planing need only to be ground after coming from the smith. Hackney states that tool steel containing 1·1 per cent. tungsten made excellent turning tools and punches. Dr. Werner Siemens has shown that tungsten steel is twice as powerful in retaining permanent magnetism as the best ordinary steel.

Chromium readily alloys with iron, producing a fine close grained steel, somewhat similar in many of its properties to tungsten steel. The finest steel for purposes of tools and cutlery, however, appears after all to be the old carbon steel; and the maximum of hardness and toughness combined is to be obtained only by selecting material as free as possible from all foreign elements, except carbon.

Sir J. Whitworth has succeeded in condensing fluid steel by the application of enormous pressure, so as to obliterate the blow holes usually contained, and has thereby produced a material having great strength, which is suitable for many special purposes. The material is of great utility for guns, linings of cylinders, &c., and the operations, though extremely difficult, have been devised with great skill; but the process is a very costly one, and the utmost that can be done is to entirely destroy all blow holes. If these can be prevented by improving the metallurgical processes, without at the same time producing a weaker metal absolutely, it would appear that compression would be needless. The specific gravity of the cast-metal should indicate whether the blow holes have been thoroughly obliterated, and it is curious that some of the samples of solid cast steel from Terre Noire show quite as high a specific gravity as Whitworth's compressed steel. According to Dr. Percy the specific gravity of Whitworth's steel is 7·84, while the Terre Noire cast metal has a density of 7·8 to 7·9. It must be admitted, however, that the elasticity of the annealed cast metal of Terre Noire is not equal to that of Whitworth's steel of the same tensile strength; but there is great hope that even this defect may be overcome, and that metallurgy will not be outdone by mechanics.

Mechanical Properties of Steel.—The resistance te crushing strain, tensile strain, elasticity, resistance to bulging stress, and other mechanical properties of steel, vary mainly according to the chemical composition of the material; but they also vary with the mode of treatment which the material has undergone. Very elaborate experiments have been made from time to time to elucidate this subject; but we are still wanting a perfectly systematized set of results, accompanied at the same time with a complete history of the processes the material has gone through, together with careful chemical and physical analyses of the material. Great expectations were formed of the value of the results that would follow from the investigations of the committee of experts appointed recently by the United States; and it will be a great pity if their labours are cut short for want of funds. D. Kirkaldy has undoubtedly made more mechanical tests of steel than any other man, and he has shown great skill in designing the apparatus for carrying these out, and indomitable perseverance in checking all his results personally with the greatest care; but the mass of results which he has accumulated requires much sifting, and his mechanical tests have unfortunately rarely been accompanied with any chemical or physical examination of the materials. They are therefore, like many others, of little use to the investigator, and seldom help us to elucidate principles.

An extremely interesting series of experiments with steel for shipbuilding purposes was made by J. Barba, chief constructor for the French navy, and reported in *Engineering* for 1875. One of the chief subjects of discussion, in reference to the extended use of steel for constructive purposes, has been the relative effects of punching and drilling upon steel plates, and Barba thus sums up his results.

"The following conclusions may be deduced from the preceding experiments on plates from ·275 to ·472 inches thick:—

"1. That the effects of punching and shearing are entirely local, and extend over a limited zone, less than ·04 inch in width on the edge of the side sheared, or of the hole punched.

"2. That no cracks exist in parts so changed.

"3. That tempering destroys the effect of shearing and of punching, by restoring the metal to the condition in which it would have been if the opera-

tion of shearing and punching had been replaced by planing and drilling.

"4. That annealing by itself or after tempering, negatives, like tempering, the alteration produced by shearing and punching.

"These various results are easily explained. The shearing and punching machines produce in the neighbourhood of the parts subjected to their action a local and extreme pressure. On the one hand, the limit of elasticity of the metal is exceeded, and it must fail to show the original extension before rupture; but this does not explain the increase observed in the hardness and tenacity.

"On the other hand, this pressure induces the solution of the combined carbon (? Ed.), and produces an actual tempering in the part acted upon by the shears and around the punch. These portions thus acquire greater hardness, more tenacity, and are susceptible of only slight extension. The temper thus produced is more intense than that obtained by sudden cooling. The pressure of the punch is sufficient to exceed the limit of resistance of the metal, and this effect can never be produced by tempering mild steel of small volume by means of simple cooling; in this latter case the pressure and the effect it produces are considerably less. It is thus that a ring surrounding a drilled hole, and tempered by sudden cooling, gave a very different result than was obtained by rings surrounding holes punched in the same plate."

The well-known and much-discussed effect of punching and shearing in reducing the strength of steel is thus clearly traced to an alteration in the metal within certain limits of the area of compression, whereby a portion of the steel is strained beyond its power of endurance, and thus a weak point is set up from whence a fracture may the more easily be started. The same reasoning explains why a piece of steel plate of medium hardness with the edge as it leaves the shears may be bent double without cracking, if it be doubled on itself in such a way that the face upon which the shear blade descended be bent inwards, while if it be bent outwards the plate will crack. In the first case the edge which has been strained beyond its limit of extension is brought inside the bend, and is therefore not subject to further extension, as it is if this portion is made to form the outside of the bend.

The experiments of BARBA were made with the mild steel of recent manufacture, produced by adding ferro-manganese to the decarburized metal instead of spiegeleisen; and the results were found to be very similar whether Bessemer or Siemens steel were used. The chemical analysis of the metal under treatment is not given; but as the tensile strain was about 28 tons per inch, it is probable that the carbon was not much above ·15 per cent.

The celebrated Creuzot works publish the following classification of their steel, which will give a good general idea of the mechanical properties of steel of various tempers and qualities. — *Engineering*, 1875, p. 119.

TABLE XV.—CLASSIFICATION OF CREUZOT STEEL.

Number of Classification.	A Class.					
	Non-Tempered.			Tempered.		
	Load Corresponding to		Percentage of Extension at Rupture.	Load Corresponding to		Percentage of Extension at Rupture.
	Rupture.	Elastic Limit.		Rupture.	Elastic Limit.	
	Tons per Square Inch.	Tons per Square Inch.		Tons per Square Inch.	Tons per Square Inch.	
1	48·31	24·72	13	74·16	45·64	·2
2	46·67	23·96	15	70·05	43·30	4·8
3	44·57	23·07	17	66·95	41·71	7·2
4	43·61	22·12	19	61·37	38·42	9·4
5	39·81	21·04	21	56·17	35·63	11·1
6	36·77	19·65	23	49·89	31·90	13·2
7	33·72	18·25	25	43·49	27·77	14·6
8	31 19	16·86	27	38·80	23·96	18·0
9	28 53	14·26	29	35·63	21·30	21·0
10	—	—	—	—	—	—
11	—	—	—	—	—	—

Number of Classification.	B Class.					
	Non-Tempered.			Tempered.		
	Load Corresponding to		Percentage of Extension at Rupture.	Load Corresponding to		Percentage of Extension at Rupture.
	Rupture.	Elastic Limit.		Rupture.	Elastic Limit.	
	Tons per Square Inch.	Tons per Square Inch.		Tons per Square Inch.	Tons per Square Inch.	
1	49·26	26·05	13	75·64	48·06	3·8
2	47 49	25·36	15	72·91	47·87	5·7
3	45·52	24·88	17	68·47	45·01	7·8
4	36·90	23·74	19	62·76	41·46	10·2
5	40·83	22·70	21	57·70	39·37	12·6
6	37·85	21·42	23	51·99	34·87	14·8
7	34·87	20·16	25	46 79	31·57	17·0
8	32·01	18·76	27	41·72	28·34	19·5
9	29·60	17·43	29	37·28	25·36	22·0
10	26·18	14·96	32	32·84	20·92	24·2
11	—	—	—	—	—	—

TABLE XV.—(*Continued.*)

Number of Classification.	C Class. Non-Tempered. Load Corresponding to Rupture.	Non-Tempered. Load Corresponding to Elastic Limit.	Non-Tempered. Percentage of Extension at Rupture.	Tempered. Load Corresponding to Rupture.	Tempered. Load Corresponding to Elastic Limit.	Tempered. Percentage of Extension at Rupture.
	Tons per Square Inch.	Tons per Square Inch.		Tons per Square Inch.	Tons per Square Inch.	
1	50·08	27·39	13	77·98	53·89	·5
2	48·31	26·75	15	75·00	51·99	6·6
3	46·40	25·99	17	71·00	49·45	8·6
4	44·25	25·23	19	66·44	45·96	10·8
5	44·78	24·28	21	62·76	43·62	13·3
6	38·99	23·14	23	56·93	39·43	16·0
7	35·00	22·06	25	51·48	36·08	18·2
8	33·09	20·73	27	46·02	34·46	20·6
9	30·56	19·46	29	40·45	28·72	23·4
10	27·58	17·62	32	33·73	23·58	27·6
11	24·92	15·47	35	29·16	20·79	33·0

TABLE XVI.—TESTS OF WEST CUMBERLAND BESSEMER STEEL PLATE, BY D. KIRKALDY, FOR THE BOARD OF TRADE.

LENGTHWAY.

Stamped.	Thickness.	Stress. Elastic Per sq. Inch.	Stress. Ultimate Per sq. Inch.	Ratio of Elastic to Ultimate.	Contraction of Area at Fracture.	Extension, Set in 10 Inches, At 50,000 lbs. Per sq. Inch.	Extension, Set in 10 Inches, At 60,000 lbs. Per sq. Inch.	Extension, Set in 10 Inches, Ultimate.	Appearance at Fracture.
	Inch.	Tons.	Tons.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
Admiralty steel, A,	·25	20·7	29·8	69·3	54·4	2·60	8·02	23·2	100 per cent. silky.
" B,	·25	20·5	30·2	67·6	57·6	3·30	7·51	25·7	"
Boiler steel, C, ...	·25	19·6	29·2	66·6	39·2	3·67	9·55	21·1	"
" W, ...	·25	22·1	32·7	67·6	47·6	0·27	5·32	23·6	"
Mean, ...	.....	20·7	30·5	67·8	49·7	2·46	7·60	23·4	
Admiralty steel, A,	·49	16·0	27·7	57·5	50·7	5·52	13·9	27·3	100 per cent. silky.
" B,	·49	16·0	27·8	57·5	48·7	5·51	13·8	29·7	"
Boiler steel, C, ...	·50	18·6	31·7	58·6	45·1	2·49	5·62	25·4	"
" W, ...	·49	19·3	32·1	60·2	40·5	2·29	5·01	22·6	"
Mean, ...	.....	17·5	29·8	58·4	46·2	3·95	3·35	26·2	
Admiralty steel, A,	·75	15·0	27·6	54·1	49·6	6·09	15·0	30·2	100 per cent. silky.
" B,	·75	15·2	28·0	54·0	52·6	5·78	14·2	31·8	"
Boiler steel, C, ...	·79	14·1	26·7	52·9	32·2	6·27	19·1	23·0	"
" W, ...	·77	17·6	30·9	57·1	24·8	2·80	6·21	17·8	"
Mean, ...	.....	15·5	28·3	54·5	39·8	5·23	13·62	25·7	

CROSSWAY.

Stamped.	Thickness.	Stress. Elastic Per sq. Inch.	Stress. Ultimate Per sq. Inch.	Ratio of Elastic to Ultimate.	Contraction of Area at Fracture.	Extension, Set in 10 Inches, At 50,000 lbs. Per sq. Inch.	Extension, Set in 10 Inches, At 60,000 lbs. Per sq. Inch.	Extension, Set in 10 Inches, Ultimate.	Appearance at Fracture.
	Inch.	Tons.	Tons.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
Admiralty steel, A,	·25	21·2	30·7	69·1	37·4	0·73	6·45	22·7	100 per cent. silky.
" B,	·25	21·5	30·9	69·1	41·4	0·53	6·03	23·0	"
Boiler steel, C, ...	·25	21·2	30·4	69·9	45·0	0·68	6·40	23·9	"
" W, ...	·25	22·0	32·2	67·9	20·4	0·41	4·44	19·1	"
Mean, ...	.....	21·5	31·0	69·0	36·0	0·59	5·83	22·2	
Admiralty steel, A,	·48	17·2	28·3	60·6	40·0	4·97	11·80	26·8	100 per cent. silky.
" B,	·48	17·1	28·2	60·4	43·5	5·26	12·70	29·4	"
Boiler steel, C, ...	·50	20·0	31·6	63·1	27·8	1·77	5·52	22·5	60 per cent. silky, 40 per cent. granular.
" W, ...	·49	20·2	32·7	61·7	23·7	1·53	4·74	17·2	80 ℔ silky, 20 ℔ granular laminæ.
Mean, ...	.....	18·6	30·2	61·4	33·7	3·38	8·69	23·9	
Admiralty steel, A,	·75	15·9	28·3	56·0	42·4	6·00	14·75	28·2	100 per cent. silky.
" B,	·74	16·0	28·3	56·3	45·2	5·80	13·57	29·8	"
Boiler steel, C, ...	·80	14·5	28·1	51·6	53·0	5·94	13·85	32·4	"
" W, ...	·77	16·8	30·7	54·9	34·2	3·14	7·29	25·3	90 per cent. silky, 10 per cent. granular.
Mean, ...	.....	15·8	28·8	54·7	43·7	5·22	12·36	28·9	

The above tests of English material, from the West Cumberland Iron and Steel Company, were made by KIRKALDY for the Board of Trade (see Table XVI. "A summary of the results of experiments to ascertain the elastic and ultimate tensile strength of twelve steel plates, annealed, received direct from Messrs. West Cumberland Iron and Steel Company, Limited." Nominal thickness, quarter, half, and three-quarter inch.) All test pieces were taken from plates of ordinary manufacture, selected by the chief engineer of the Board of Trade. The steel was made by the Bessemer process, a mixture of ferro-manganese and spiegeleisen being used. The ingots were hammered into slabs about 6 inches thick, reheated and rolled into plates at one heat. The annealing was done in a Siemens furnace.

The analyses of these plates gave the following results:—

	Cast A	B	C	W
Iron,.....	99·274 ..	99·099 ..	99 550 ..	99·036
Carbon,.....	·140 ..	·200 ..	·100 ..	·240
Silicon,.....	trace. ..	trace. ..	trace. ..	·159
Sulphur,.....	·030 ..	·046 ..	·057 ..	·040
Phosphorus,.....	·030 ..	·015 ..	·027 ..	·021
Manganese,.....	·590 ..	·640 ..	·489 ..	·504

On the whole, it will be seen that this material is of very high class, as the mean tensile strain of all the samples cut lengthways is 30 tons per square inch, and the elongation 25 per cent.; while one of the samples, with a strength of 28·1 tons, elongated 32·4 per cent. This is a greater elongation than was reached by any of the samples of the chain cable iron tested by the United States committee of experts, and reported on by HOLLEY, the best result of the whole series giving only 29·9 per cent. elongation, with a tensile strength of 24·2 tons, while the average is very far below this standard. It will be noted also that the material is nearly of the same strength and elasticity when tested crossway, in which respect it again far exceeds iron. It appears that the thinner plates give a higher tensile strain and lower modulus of elasticity than the thicker ones. This is what might be expected, although the annealing to a great extent removes the hardness produced by rolling.

In 1870 a committee of the Institute of Civil Engineers presented an elaborate and valuable report upon "The Mechanical and other Properties of Steel," from experiments made at the Woolwich Dockyard. The following table, No. XVII., is extracted to show the connection between chemical composition and mechanical properties. The analyses were performed by E. RICHARDS, of the Barrow Steel Works, and Dr. ODLING. It is to be regretted that there are serious discrepancies between the analytical results of these two chemists, which have not been cleared up, as they render it difficult to deduce conclusions from the observations.

The enormous quantities of steel now used for railway bars renders any observation upon the material employed of great consequence. Numerous observations have been made upon the effect of punching upon this kind of steel, and all investigations corroborate the statement first made by BRAMWELL, that punching or notching deteriorates such

TABLE XVII.—SHOWING THE CHEMICAL ANALYSIS AND SPECIFIC GRAVITY OF 14 BARS, WITH THE RESULTS OF EXPERIMENTS ON THE ELASTICITY AND ULTIMATE STRENGTH OF THE SAME.

Description of Steel.	What the Steel was intended for.	Carbon.		Silicon.		Manganese.		Sulphur.		Phosphorus.		Graphite.		Iron.		Specific Gravity.		Ultimate tensile stress per square inch.	Yielding point. Tension.	Yielding point. Compression	Total extension of bar in parts of a foot.	Ratio of fractured to original sectional area.
		Richards	Odling.	Richards	Odling.	Richards	Odling.	Richards	Odling.	Richards	Odling.	Richards	Odling.	Richards	Odling.	Richards	Odling.	Tons.	Tons.	Tons.		
STEEL—Crucible cast steel, from Swedish bar iron, chisel temper,.....	—	·790	·980	·115	·182	·190	·211	trace.	·010	·010	·000	—	·025	98·860	98·951	7·839	—	52·76	26·00	26·33	·5290	·943
Crucible cast steel,.....	—	·670	·805	·200	·270	·440	·216	trace.	·020	·020	·000	—	·113	98·670	98·574	7·831	—	51·01	25·50	26·17	·7296	·800
Cast steel,.....	—	·570	·612	·140	·148	·370	·272	·010	·009	·040	·000	—	·090	98·870	98·867	7·851	—	43·48	26·00	25·50	·4685	·948
"	Tyres,	·900	—	none.	—	·390	—	·020	—	·060	—	—	—	98·630	—	7·844	—	41·85	27·00	26·00	·1093	1·000
Crucible steel,.....	Piston rods, &c.,	·580	—	·220	—	·300	—	·020	—	·010	—	—	—	98·870	—	7·825	—	40·50	20·50	18·00	·4134	·959
"	—	·470	—	none.	—	·610	—	·020	—	·020	—	—	—	98·880	—	7·845	—	38·51	16·83	16·17	·7916	·957
Hammered crucible c. steel,	Gun barrels,	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	37·05	25·00	24·00	·1315	·985
Crucible cast steel,.....	Axles,rails,&tyres	·590	·253	·030	·036	·140	·120	trace.	·006	·020	·000	—	·095	99·220	99·486	7·859	—	—	—	21·00	—	—
Crucible steel,.....	—	·440	—	·140	—	·230	—	·010	—	·020	—	—	—	99 160	—	7 850	—	35·47	20·00	20·50	·9636	·513
Bessemer steel,.....	Fge. ham.&rolled.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	35·40	19·50	18·00	1·1135	·558
"	Axles,rails,&tyres	·340	—	trace.	—	·350	—	·040	—	·030	—	—	—	99·240	—	7·857	—	—	—	22·50	—	—
"	—	·320	—	·010	—	·400	—	·040	—	·020	—	—	—	99·210	—	7·857	—	34·19	20·00	21·17	1·1899	·544
"	—	·310	·393	·050	·131	·380	·181	·020	·051	·020	·000	—	·022	99·220	99·238	7·853	—	33·68	17·50	16·00	1·1456	·808
"	Tyres and axles,	·350	—	·0·0	—	·440	—	·040	—	·010	—	—	—	99·130	—	7·852	—	33·66	16·83	15·83	1·3593	·588
Cast steel,.....	Piston rods, &c.,	·520	—	·100	—	·190	—	trace.	—	·030	—	—	—	99·160	—	7 850	—	33 65	26·75	27·00	·0865	·987
Rolled crucible cast steel,	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	34·43	20·50	24·00	·2018	·971
IRON FOR COMPARISON—																						
Lowmoor iron,.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	28·88	14·00	13·33	·6978	·941
Yorkshire iron,.....	—	·320	—	·100	—	·080	—	·020	—	·080	—	—	—	99·490	—	7·758	—	23·69	13·17	13·00	1·7847	·486

steel to a very great extent. According to C. P. Sandberg, mild steel rails are weakened 80 per cent. by notching in the flange, and hard steel rails 97 per cent. by square cornered notches $\frac{1}{4}$ inch deep, and 95 per cent. by round cornered notches. Hackney states that a Great Western double-headed rail with no holes stood a blow of 1 ton falling 20 feet, while, when a hole was punched through the web, it broke under the first blow with a 3 feet fall; and when the hole was drilled it stood a 2 feet fall, but broke with the second blow from 4 feet. Price Williams had an elaborate series of tests, conducted by Kirkaldy, upon the same point (see paper on "Permanent Way of Railways," Inst. C.E.), and arrived at the conclusion that "the ultimate stress of steel rails punched cold in the ordinary way was 65·39 per cent. of the ultimate stress of unpunched rails, whereas the ultimate stress of the drilled rails was 98·68 per cent. of that of the undrilled rails." This was, of course, with a gradually applied strain. Williams has also investigated with great care the wear of steel rails, and has proved conclusively that a rail rolled from a cogged ingot is stronger than a rail of the same steel from a hammered ingot.

Two of the first steel rails ever used on a railway were laid on the London and North Western line at Camden Town; and, according to Price Williams' calculation, one of these carried 5,152,856 tons for each one-sixteenth of an inch worn down, the other 8,474,576 tons for one-sixteenth of an inch wear; while on an average the Crewe rails require 9,370,777 tons to roll over them before they lose one-sixteenth of an inch in thickness; while some steel rails on the Great Eastern Railway have withstood 27,000,000 tons, and on the Great Northern Railway, 30,000,000 tons for each one-sixteenth of an inch wear. It appears that the character of the ground has more to do with the wear of a steel rail than anything else. If the ballast be continually wet, the rail gets ground out very rapidly, while in dry situations, where dust and dirt do not aid the grinding action of the wheels, they are extremely durable. Williams assumes 43 years as the average life of steel rails. The following extremely interesting table (XVIII.) of the wear of rails on the Great Northern Railway is also due to Williams, and is highly instructive. The whole paper will well repay a close study:—

TABLE XVIII.—SUMMARY OF TABLE SHOWING THE AMOUNT OF WEAR AND TONNAGE OVER STEEL RAILS IN AND NEAR MAIDEN LANE AND COPENHAGEN TUNNELS, TOGETHER WITH A CHEMICAL ANALYSIS OF THE RAILS.

No. 9. Copenhagen Tunnel. (Down.)	No. 17. Maiden Lane Tunnel (up).	No. 18. Maiden Lane Tunnel. (Up.)	No. 21. North of Copenhagen Tunnel (up).	No. 22. North of Copenhagen Tunnel (up).	No 23. North of Copenhagen Tunnel (up).	No. 24. North of Copenhagen Tunnel (up).
Tonnage. 96,824,000	Tonnage. 40,329,000	Tonnage. 40,329,000	Tonnage. 63,868,000	Tonnage. 63,868,000	Tonnage. 59,638,000	Tonnage. 59,638,000
Tonnage per 1-16th Wear. 15,129,000	Tonnage per 1-16th Wear. 5,251,000	Tonnage per 1-16th Wear. 8,402,000	Tonnage per 1-16th Wear. 7,676,000	Tonnage per 1-16th Wear. 9,283,000	Tonnage per 1-16th Wear. 15,531,000	Tonnage per 1-16th Wear. 31,061,000

CHEMICAL ANALYSIS BY RILEY.

	No. 9. Copenhagen Tunnel (down).	No. 17. Maiden Lane Tunnel (up).	No. 18. Maiden Lane Tunnel (up).	No. 21. North of Copenhagen Tunnel (up).	No. 22. North of Copenhagen Tunnel (up).	No. 23. North of Copenhagen Tunnel (up).	No. 24. North of Copenhagen Tunnel (up).
Carbon,	0·336	0·331	0·296	0·302	* 0·538	0·340	† 0·270
Silicium,	0·034	0·029	0·029	0·034	0·040	* 0·062	† 0·020
Sulphur,	† 0·038	0·090	0·051	* 0·096	0·059	0·055	0·051
Phosphorus,	0·125	0·186	0·144	0·162	0·111	* 0·242	† 0·100
Iron,	99·408	99·451	99·637	99·632	99·249	99·223	99·475
Manganese,	0·338	0·353	† 0·245	† 0·245	0·461	* 0·475	0·259
Copper,	* 0·052	0·020	0·020	† 0·018	0·022	0·028	0·025
	100·311	100·460	100·422	100·489	100·480	100·425	100·200

* Maximum percentage. † Minimum percentage.

Smith of Barrow has likewise investigated the question of wear of steel rails, and has come to the remarkable conclusion that it is not the hardest rails, or those highest in carbon, which wear the longest. This conclusion seems to be confirmed by the previous table, although contrary to what might have been expected. Further experiments and observations upon these points would be desirable. The following table (XIX.), by Smith, is the foundation for his deductions.

A comparison of the tensile strength and elasticity of mild steel, as compared with the best Yorkshire brands of iron, such as Lowmoor and Bowling, shows the great superiority of the former in every respect; and as steel can now be made of thoroughly reliable and regular quality at about half the cost of this far-famed material, there would appear to be no object in adhering to the more expensive material; and as prejudice wears away there is every reason to expect that steel will supersede iron for shipbuilding, bridge construction, and boiler work, as completely as it has already superseded iron for railway bars.

Much greater progress is being made in the use of steel in France and Germany than in England, the Governments of these countries lending valuable assistance to the manufacturers: 40, 50, and even 100 ton castings are now common in France, and Terre Noire is making guns and armour plates from annealed castings without hammering or rolling.

TABLE XIX.—RESULTS OF EXPERIMENTS ON DOUBLE-HEADED BESSEMER STEEL RAILS, MANUFACTURED AT THE BARROW WORKS, IN WEAR ON THE MAIN LINE OF THE FURNESS RAILWAY FOR EIGHT YEARS.

No.	Strain required to punch hole ⅞-inch diameter through web ½-inch thick.	Bending strain required to produce permanent set. Supports 36 inches apart.	Tensile Tests. Specimens from Web.		Carbon.	Original weight of rail per yard.	Weight of rail per yard after wear.	Wear of rail per yard.	Percentage of wear.	
			Breaking strain per square inch original sectional area.	Elongation. Length extended = 2 inches.						
	Tons.	Tons.	Tons.	Per Cent.	Per Cent.	Lbs.	Lbs.	Lbs.		
1	46·25	19	30·91	37·5	0·28	73	63·41	9·59	13·13	Soft rails. Average wear, 13·54 per cent.
2	46·33	19	30·08	36·5	0·28	73	63·93	9·07	12·42	
3	46·97	19	31·03	36·0	0·28	73	63·95	9·05	12·39	
4	47·18	19	31·56	35·0	0·28	73	64·84	8·16	11·17	
5	48·21	20	31·53	36·0	0·29	73	61·52	11·48	15·72	
6	48·27	20	32·85	34·5	0·30	73	63·26	9·74	13·34	
7	48·50	20	33·37	32·0	0·30	73	61·14	11·86	16·24	
8	48·86	20	33·07	32·0	0·29	73	63·11	9·89	13·55	
9	48·89	20	31·88	36·0	0·31	73	63·02	9·98	13·67	
10	49·00	20	32·33	37·0	0·29	73	62·30	10·70	14·66	
11	49·00	20	33·37	34·0	0·31	73	65·07	7·93	10·86	
12	49·07	20	32·09	37·0	0·30	73	62·34	10·66	14·60	
13	49·41	20	31·97	33·5	0·32	73	65·46	7·54	10·33	
14	49·50	20	32·75	32·0	0·31	73	64·02	8·98	12·30	
15	49·68	21	33·18	32·5	0·29	73	61·66	11·34	15·53	
16	50·00	21	33·59	36·0	0·30	73	61·61	11·39	15·60	
17	50·11	21	33·08	35·0	0·30	73	61·37	11·63	15·93	
18	50·27	21	32·67	35·0	0·30	73	62·67	10·33	14·15	
19	51·05	21	33·65	32·0	0·32	73	63·60	9·40	12·87	
20	52·50	21	33·49	32·0	0·32	73	64·00	9·00	12·33	
21	56·79	23	37·01	26·0	0·36	73	58·01	14·99	20·53	Hard rails. Average wear, 15·18 per cent.
22	58·16	23	37·42	26·0	0·40	73	59·95	13·05	17·87	
23	58·44	23	37·93	23·0	0·40	73	63·51	9·49	13·00	
24	61·24	24	41·41	26·0	0·39	73	60·45	12·55	17·19	
25	61·34	24	39·10	22·0	0·43	73	64·24	8·76	12·00	
26	64·42	24	42·82	25·0	0·44	73	63·66	9·34	12·79	
27	65·19	26	44·00	16·5	0·45	73	63·36	9·64	13·20	
28	65·31	25	39·23	24·0	0·44	73	60·84	12·16	16·66	
29	74·50	28	45·79	3·0	0·50	73	62·68	10·32	14·14	
30	82·47	31	50·42	3·0	0·57	73	62·44	10·56	14·47	

SUGAR.—*Sucre*, French; *Zucker*, German. Of the many varieties of sugar there are but three of any commercial importance—viz., cane sugar or saccharose, grape (or starch) sugar or dextrose, and the so-called fruit sugar or lævulose, which accompanies dextrose in those varieties of brewing sugar which are prepared from cane sugar. Of these saccharose is by far the most important, and will alone be treated on under the head SUGAR.

"Cane" sugar occurs in a very large number of plants, but is only manufactured from sugar-cane, sugar-beet, sorghum, a species of palm tree, and sugar-maple. It is absolutely the same substance, as far as can be determined by any known means, whether it be obtained from one source or the other; and being in an equally pure state, has the same sweetening power. It, like all sugars, is composed of the elements carbon, hydrogen, and oxygen, which in this case are united in such proportions that there are 12 times 12 parts of carbon, or C_{12}; 22 times 1 part of hydrogen, or H_{22}; 11 times 16 parts of oxygen, or O_{11}; so that the formula which represents its composition is $C_{12}H_{22}O_{11}$.

It crystallizes from its solutions in water or dilute alcohol in anhydrous (without water of crystallization) crystals, belonging to the monoclinic (singly oblique) system, which can be grown to a large size by suspending them in a slightly supersaturated solution of sugar, and allowing the whole to stand at rest for a long time. The specific gravity of the pure crystals is 1·606. It is soluble in one-third of its weight of cold water, and is even more soluble at higher temperatures. At the boiling point of water the concentrated solution becomes syrupy.

SCHEIBLER gives the following solubilities in alcohol at 14° C. He also gives (*Zeitschrift des Vereins für die Rübenzucker-Industrie*, xxii. p. 246) the solubilities at 0° C. and 40° C.:—

Volume Per Cent. Alcohol.	Solubility of Sugar in Aqueous Spirit at 14° C.	
	100 c.c. of the Saturated Solution contain	Specific Gravity of the Saturated Solution.
	Grams. Sugar.	
0	85·8	1·3248
5	82·4	
10	79·4	1·2991
15	76·5	
20	73·4	1·236
25	69·8	
30	66·0	1·2293
35	61·6	
40	56·7	1·1823
45	51·6	
50	45·7	1·1294
55	39·6	
60	32·9	1·050
65	25·6	
70	17·8	0·9721
75	11·2	
80	6·4	0·8931
85	2·7	
90	0·7	0·8369
95	0·2	
97·4	0·08	0·8062
100	0·00	

The same authority, as the result of his own determination, gives the percentage of sugar contained in the solutions saturated at—

	Per Cent.
0° C. (32° Fahr.),	65
5° C. (41° Fahr.),	65·2
10° C. (50° Fahr.),	65·6
15° C. (59° Fahr.),	66·1
20° C. (68° Fahr.),	67·0
25° C. (77° Fahr.),	68·2
30° C. (86° Fahr.),	69·8
35° C. (95° Fahr.),	72·4
40° C. (104° Fahr.),	75·8
45° C. (113° Fahr.),	79·2
50° C. (122° Fahr.),	82·7

Sugar, like many other organic bodies of complex constitution, has the power, even when in solution, of rotating or twisting the plane of a ray of polarized light; and the amount or degree of rotation which it causes is proportional to the number of molecules of sugar acting on the ray. Thus, if we pass a ray of polarized light through 100 millimetres of a solution of pure sugar, containing 10 grams. of sugar in 100 c.c., that ray will be twisted to the right (hence sugar is called dextro-rotatory) into a plane at an angle of $n°$ to its former one; but if we double the length of the column of sugar solution, or double the quantity of sugar, the length remaining the same, we double the number of acting molecules, and so double the rotation. This fact obviously furnishes us with a method of estimating the amount of sugar in any transparent liquid not containing any other optically active substance.

The instruments by which this rotation of the plane of polarization is observed are called polariscopes or saccharometers, and take three principal forms. The first, or "Soleil-Duboscq" instrument, especially as improved by SCHEIBLER, is a good instrument for the use of those who have a keen perception of slight differences of shades of colour, but is quite useless to any one at all colour-blind—for whom, as indeed for most people, the instruments known as the Cornu-Jellet polariscope, or *saccharimeter à penombres*, or LAURENT'S modification of it, are to be strongly recommended. Space fails in which to describe the construction of these various instruments; and their manipulation, so far as it needs description, will be found under the head *Estimation of Sugar*.

When heated in solution with dilute acids, or when submitted to the action of ferments for a limited period, sugar takes up the elements of water, H_2O, and splits into two molecules of different glucoses—viz., dextrose, which has a right-handed rotatory power for polarized light; and lævulose, which is lævo-rotatory. Both have the same formula—$C_6H_{12}O_6$—but differ considerably in their properties, doubtless owing to a different arrangement among themselves of the atoms, or groups of ultimate particles, of which the respective molecules consist. Because the lævulose rotates to the left more strongly than the dextrose to the right, the mixture rotates to the left, or the rotatory action of the original cane sugar has been inverted; whence the name "invert sugar" commonly applied to this mixture. Long boiling with water gives rise to the same result to a slight extent; but if both sugar and water be pure and free from all acids, it is to a slight extent only. It has been stated that an aqueous solution of sugar, when exposed to light, undergoes inversion, but this is not correct. In the *absence of ferment germs* solutions of sugar will keep unaltered, not only for months, but for years.

The *inversion* of cane sugar is accomplished by different acids with very various degrees of rapidity. DUBRUNFAUT states that one *equivalent* of sulphuric acid (49 parts) has only half as great a power of inversion as one of hydrochloric acid (36·5 parts), and at 100° C. (212° Fahr.), $\frac{1}{10000}$th of tartaric acid causes complete inversion. He further states that if one-half the inversion takes place in the unit of time, in the next unit only one-half as much sugar is inverted, and in the next one-quarter; or, in other words, the action of the acid is proportional to the number of molecules of sugar on which it has to act. The time required for a given amount of inversion is, roughly speaking, in inverse proportion to the quantity of acid, the concentration, &c., remaining the same; but these statements are contradicted, as regards their quantitative parts, by more than one respectable authority.

Weak acids, such as acetic and some other vegetable acids, possess very little power of "inversion" at any temperature short of 100° C.; and accordingly when sulphuric or hydrochloric acids are added to concentrated cane or beet juice, as is done in Demerara, and of late in France by MARGUERITE, the natural vegetable acids are displaced and set free by the stronger mineral acids, which become neutralized by the bases with which the former were originally combined. The free *vegetable acids*, though making the liquid very sour, invert but little sugar at the temperature at which the solution boils *in the vacuum*. For a very interesting and important paper on the inversion of sugar by acids consult A. BEHR in STAMMER'S "Jahres-Bericht über die Untersuchungen und Fortschritte der Zuckerfabrikation" for the year 1874.

Though sugar is so easily inverted by acids, it withstands the action of alkalies very perfectly—a solution mixed with caustic potash, soda, or lime, and boiled, even, undergoes no change of colour if free from glucose; and though, *while alkaline*, it exhibits diminished rotatory power for polarized light, it recovers its original power on being neutralized. Sugar, indeed, forms many compounds with the alkalies and alkaline earths to which formulæ have been given, though they are so difficult or impossible to prepare in a pure state that their accurate composition cannot be said to be in all cases determined. The potassium and sodium compounds are made by adding strong alcohol to a solution of sugar and potash, or soda, respectively. They are both gelatinous precipitates, difficult to wash with alcohol, and affording no guarantee of purity. The formulæ assigned to them are $C_{12}H_{21}KO_{11}$, and $C_{12}H_{21}NaO_{11}$, which are improbable. The barium compound is the one which is most definite in its characters; it is easily obtained in a crystalline condition by boiling down a solution of sugar mixed with a large quantity of caustic baryta (or sulphide

of barium) until a sandy precipitate settles out. This must then be washed with water free from carbonic acid, in an atmosphere also free from the same impurity. The formula indicated by the analysis of the compound so prepared is $C_{12}H_{22}O_{11}BaO$. The easy formation and purification of this body have led to its being employed on a large scale as a means of recovering sugar from molasses; for when prepared and washed it needs only to be decomposed by carbonic acid in order to set free the sugar, which can then be obtained in the solid form by evaporation. The removal of the last portions of the poisonous baryta from the solution is easily effected by gypsum, which, of course, throws it down as insoluble sulphate. The process is due to DUBRUNFAUT.

The lime compounds, though very important technically, are unfortunately rather indefinite in their characters, and it is almost impossible to purify them so that a really satisfactory analysis can be made. Accordingly, the most contradictory statements are current; but the balance of evidence seems to point to the existence of two definite compounds—$C_{12}H_{22}O_{11}CaO$, monobasic sucrate of lime, corresponding to the definite barium compound, and $C_{12}H_{22}O_{11}3CaO$, tribasic sucrate of lime. The first is made by dissolving lime in sugar solution in such quantity that it is rather below than above the theoretical amount, filtering the strongly alkaline solution, and precipitating by the addition of alcohol. It is soluble in water, is strongly alkaline, and absorbs carbonic acid greedily.

The tribasic sucrate is only slightly soluble, and is much less so in hot than in cold water; accordingly, if any solution of lime in sugar-water be heated tribasic sucrate will be formed, and if the solution is not too dilute, or does not contain too large a proportion of sugar to lime (so as to forcibly maintain the monobasic sucrate in existence), it will separate in a more or less gelatinous form, which gives the appearance of coagulation, such as occurs with white of egg.

A cold solution of sugar lime rapidly absorbs carbonic acid passed into it, but remains quite clear up to the point where about one-half of the lime is combined with carbonic acid; then the liquid suddenly becomes opalescent, and, if sufficiently concentrated, gelatinous throughout. On continuing the passage of the gas the pasty mass becomes thinner and thinner as the carbonate of lime becomes more and more crystalline, and in the end there is obtained a clear solution of sugar and a sandy precipitate of carbonate of lime. The gelatinous precipitate which is formed at one stage is in all probability merely a hydrated carbonate of lime, possibly containing an excess of base, and, consequent on its physical character, entangling and retaining a certain proportion of whatever is in solution (*e.g.* the sugar) when it was formed. BOIVIN and LOISEAU supposed the jelly to be a definite chemical compound of sugar lime and carbonic acid, and called it hydro-sucro-calcic-carbonate, but no one has been able to verify the analytical data. At any rate, this jelly is easily formed on the large scale, and is applied, as described further on, to the purification of raw sugar in the Boivin and Loiseau process, known also as the Tooth process when applied to cane juice.

SOLUBILITY OF LIME IN SUGAR SOLUTIONS.

Quantity of Sugar Dissolved in 100 parts of Water.	Density of Syrup.	Density of Syrup when Saturated with Lime.	100 parts of Residue dried at 120° contain	
			Lime.	Sugar.
40·0	1·122	1·179	21·0	79·0
37·5	1·116	1·175	20·8	79·2
35·0	1·110	1·166	20·5	79·5
32·5	1·103	1·159	20·3	79·7
30·0	1·096	1·148	20·1	79·9
27·5	1·089	1·139	19·9	80·1
25·0	1·082	1·128	19·8	80·2
22·5	1·075	1·116	19·3	80·7
20·0	1·068	1·104	18·8	81·2
17·5	1·060	1·092	18 7	81·3
15·0	1·052	1·080	18·5	81·5
12·5	1·044	1·067	18·3	81·7
10·0	1·036	1·053	18·1	81·9
7·5	1·027	1·040	16·9	83·1
5·0	1·018	1·026	15·3	84·7
2·5	1·009	1·014	13·8	86·2

Other bases, such as magnesia, lead oxide, iron oxide, &c., combine with sugar to form soluble compounds. Little is known about them, and to the manufacturer or refiner they are of little importance, except in so far that his syrups, &c., will dissolve and become contaminated with lead or iron if allowed to pass through rusty or scaly pipes or cisterns of those metals.

Sugar has the power of uniting with several salts to form a number of definite crystalline compounds. A close study of these bodies throws much light on the influence of "salts" in interfering with the crystallization of sugar and promoting the formation of molasses. As common salt is the most common saline impurity, the compounds which it forms are the most important.

When sugar is mixed with so much salt as will form about 14 per cent. of the whole mass, and the two are then dissolved together, filtered, rendered slightly alkaline to prevent fermentation, and the solution set aside to evaporate slowly in a warm place, a viscid, somewhat treacly liquid is formed, in which slowly, but very slowly, crystals having the form of prisms with pyramidal ends are deposited, and continue to grow larger for a long time. They may be purified by solution in spirit of 10 per cent. and re-crystallization, and then have very sharply the composition represented by $C_{12}H_{22}O_{11}NaCl2H_2O$. Another compound, having the formula

$$2C_{12}H_{22}O_{11},3NaCl4H_2O$$

has also been obtained.

An iodide of sodium compound, with the composition $2C_{12}H_{22}O_{11},3NaI,3H_2O$, is easily obtained in very large crystals by gently evaporating at ordinary temperatures a solution containing the two substances in about the theoretical proportions.

Chloride of potassium and chloride of ammonium, when added to solutions of sugar, behave like common salt so far that they make the solution viscid, and prevent the deposition of crystals of pure sugar.

They also unite with the sugar, and crystallize out with it when crystals do at last form. These crystals have not a constant composition, but contain proportions of the "salt" and sugar, varying with the proportions of those bodies in solution; the crystals are anhydrous, and it is probable that the compounds in definite molecular proportions, which doubtless exist, are isomorphous with sugar itself, and consequently crystallize out along with it in all proportions. The interest of these bodies lies in the fact that their solutions are brought to crystallize with great difficulty, and that they persistently maintain a state of supersaturation in presence of even many crystals of their own composition. For after so much of the sugar of a vegetable juice has been removed by evaporation that the salts left in the mother liquors are in proportion to form all or any of the above compounds, the liquor becomes too sticky to admit of the free crystallization even of that sugar which is still uncombined with salts, and consequently a double loss occurs to the manufacturer: first, of the sugar which unites with the salts to form these compounds; and secondly, of that which is retained in solution in the practically uncrystallizable syrup so made.

The so-called third running beet sugars, which often stand in the crystallizing tanks for six months, nearly always contain large quantities of salts actually crystallized out with the sugar, mostly chloride and nitrate of potassium.

The experiments of Scheibler and Marschall to determine the molasses-forming power of certain salts were made by adding a certain quantity of a given salt to a known excess of pure sugar, together with as much water as would naturally leave a considerable proportion of sugar undissolved at the ordinary temperature. The mixtures were made in tubes, which were then sealed before the blow pipe and heated in the water till "salt" and sugar were both dissolved. The tubes were then allowed to cool, and stood aside at an even temperature for many weeks; opened, and the quantity of sugar remaining in solution, *in proportion to the water*, was determined. In some cases more and in others less was found, than if simply pure water had been used. Those salts giving rise to the first case they called "molasses-forming," and the second "negative molasses-forming," implying that their presence had caused more sugar to crystallize than otherwise would have done. But these experiments were wrongly conceived; for the question is not what proportion of the sugar present can you obtain on the *first crystallization*, but how much of the total sugar present can you recover by repeated concentration. It is certain pure sugar would give the best result.

Dry sugar melts at 160° C. (357° Fahr.) to a colourless liquid, which on cooling remains glassy for some time, and then becomes crystalline and opaque. At a little above this temperature it is said to be converted into a mixture of dextrose and lævulosan, and at about 200° C. (392° Fahr.) to lose water and become a mixture of glucosan and lævulosan, and at 210° C. (410° Fahr.) to be converted, with further loss of water, into caramel; but the evidence on which these statements are made is somewhat insufficient as regards the composition of the bodies formed, though water *is* lost and mixtures of bodies more or less brown are formed.

Analysis and Valuation of Sugar, &c.—*Reagents needed.*—The reagents required for the examination and analysis of sugars and syrups are:—

A solution of basic lead acetate.—Grind together in a mortar 1 lb. sugar of lead and ½ lb. litharge, with enough water to make the whole pasty. Dissolve in about 3 pints of boiling water, with constant shaking till all the litharge has disappeared. Filter the solution, and preserve in well-closed bottles.

A solution of sulphurous acid in water.

Sodium sulphite in crystals.

Washed alumina—made by pouring a solution of alum into an excess of a hot solution of washing soda, and washing the precipitate obtained in a linen bag by pouring boiling water continually through it. It is to be mixed with enough water to form a thin cream.

Purified Animal Charcoal.—Digest 1 lb. of ground new animal charcoal in 5 or 6 lbs. strong hydrochloric acid (the common yellow acid will do), diluted with twice its own bulk of water, at a boiling heat for some time; filter off and wash the residue in a linen bag with boiling water till the filtrate is no longer acid; dry and ignite to full redness in a covered crucible, and immediately bottle the still warm char in a number of small well-stopped bottles. It is essential that it be kept dry.

Pure hydrochloric acid.

Pure concentrated sulphuric acid.

Pure copper sulphate in crystals (this must be pure and free from adherent moisture).

Pure Rochelle salt (sodio-potassic tartrate). The commercial article sold as pure is nearly always unfit for the purpose to which this reagent is applied, and needs to be recrystallized at least once before use.

A solution of caustic soda as pure as can be obtained. Commercial caustic soda of good quality, when treated with only so much water as to dissolve about three-fourths of it, makes a solution so strong that the bulk of the impurities (sulphates, carbonates, &c.) are not dissolved, and may be filtered off through clean sand. Dilute the clear syrupy liquor to a spec. grav. of 1·14, and preserve for use. The last three reagents are used for the preparation of—

Fehling's solution for the detection and estimation of glucose. For this purpose dissolve 34·64 grams. of the copper sulphate in about 200 c.c. of water in a beaker, and pour this into a solution of 173 grams. of the Rochelle salt in 480 c.c. of the soda solution contained in a litre flask, shaking after each addition. Make up with water to the mark, and bottle off in a number of small well-stopped bottles, which *keep in a dark cupboard.* Prolonged exposure to light so alters the solution that it is decomposed on simply boiling.

To standardize this solution, prepare a solution of "invert" sugar of known strength by dissolving 0·475 grams. dry loaf sugar in about 10 c.c. water and 1 c.c. pure hydrochloric acid in a 100 c.c. flask, and heating to 70° C. for five minutes, cooling, and making up to 100 c.c. 0·475 grams. cane sugar inverted = 0·5 grams. glucose. When 10 c.c. of this solution (= 0·05 grams. glucose) are added slowly from a burette to 10 c.c. of Fehling's solution, kept boiling as described below, the latter, if of right strength, should be completely, but only just, decolorized.

Estimation of Sugar and Glucose—Preparation of the Solution for Polarization.—First obtain a fair average sample, the doing which, though the most difficult part of the analysis, needs no description. Weigh off the normal weight (16·2—26 grams., according to the polariscope employed) of the sugar to be analyzed; introduce it into a 100 c.c. flask by the help of a smooth wide-necked funnel, and water enough to rinse all down. Rather more than half fill the flask with water, and shake occasionally till *all* the sugar is in solution. This last point is most important, as any grains left would become imbedded in the precipitate next made, and might never get fairly dissolved in the bulk of the liquid. According to the quality of the sugar the solution will be "colourless but cloudy," "yellow," "brown," or almost black.

In the first case add about 3 c.c. of the creamy alumina, and one drop of the basic lead acetate. In the second case the same, but with three to five drops more of the lead solution. In the third and fourth cases add about 2 c.c. of the solution of sodium sulphite, and then basic lead acetate cautiously and with constant shaking, till no more precipitate is formed. In either case shake well, and allow the whole to stand ten minutes, to permit of the full separation of any precipitate that is to be formed; then fill up to within a short distance of the mark with water. The froth, which is almost always present, would take so long to break and allow of filling up exactly, that it is necessary to let a drop or two of spirit fall gently on the surface, which is best done by help of a small squirt bottle; this makes the bubbles disappear at once. Complete the filling to the mark with the utmost care; close the mouth of the flask with the thumb, and shake vigorously, to insure all parts of the liquid having the same composition.

It is commonly advised to add 5 to 10 c.c. of the basic lead acetate to the solution of a raw sugar for the purpose of clearing it; but any excess of this reagent dissolves some of the precipitate first formed, making an opalescent solution which filters with extreme difficulty. The above method is therefore much to be preferred. Scheibler prefers the following method of clarification, which is certainly simple and good, for all ordinary qualities of beet and cane sugars:—He prepares two reagents, one of basic lead acetate, and the other of aluminium sulphate, of such a strength that equal volumes of each, when added together, leave no sulphate in solution. To the dissolved sugar he adds 5 c.c. of each of these liquids, shakes, and makes up to 100 c.c. as above.

Some exceptionally black, or rather deep red sugars, and most beet molasses, will not yield a solution so colourless as to admit of accurate reading in a colour instrument, such as Soleil-Duboscq's or Scheibler's modification of it, by either of the above methods. In such a case weigh off double the normal quantity; clarify by the method given for low sugars, only adding a slightly greater excess of basic lead acetate; filter; measure off 50 c.c. of the filtrate into another 100 c.c. flask; add a solution of sulphurous acid till the liquid smells strongly of it, then about 2 grammes of the purified animal charcoal, shake; make up to 100 c.c., and filter. The lead sulphite formed carries some of the colouring matter down with it, the excess of sulphurous acid partially bleaches the remainder, and the char exerts great absorbent power in the acid solution; so that, as an end result, we obtain a beautifully bright lemon-yellow solution from the worst of molasses. In no case resort to filtering through a column of animal charcoal, as often advised. It is impossible to obtain correct results by such means; the char absorbs and retains sugar as well as colouring matter as long as it retains any power of decolorizing at all.

The solutions having been thus obtained, proceed to fill the tubes. It is assumed that all these have been tested as to their exact length, and are known to be correct. One cap being on, rinse out the tube with a little of the liquid to be examined; then fill up till the liquid threatens to overflow, and slide on the other glass and fasten with the cap. Loosen both caps, so that the glass discs are not subjected to any compression which might cause *them* also to exert a rotatory action on the ray, and then make the readings. The *direct* reading thus obtained will be sufficient in the case of all beet sugars, and of nearly all good cane sugar; but molasses, "concrete," and some varieties of low syrupy sugars, contain a glucose which is optically active, though less so than pure "invert sugar," which it is often supposed to be. We must in such cases resort to "inversion." For effecting this take a flask marked for 50 c.c. at the lower part of its neck and 55 c.c. in the upper part, fill to the lower mark with the liquid used for the direct polarization, drop in one or two crystals of sodium sulphite, fill to the upper mark with strong pure hydrochloric acid, transfer the liquid to a long-necked assay flask, and stand this in a bath of cold water, which is to be slowly raised to 70° C. When this temperature has been maintained for two or three minutes, stand the flask in cold water till its contents have acquired very nearly the temperature of the air. Now fill a tube (which must be of glass, provided with a lateral opening for the introduction of a small thermometer), which is $\frac{1}{10}$ths of the length of the tube used for the direct reading, and observe the rotation which is produced, noting at the same time the temperature of the liquid.

The direct reading gave the resultant of all the rotations of the plane of polarized light effected by

the optically active substances present in the solution. Assume that these consisted of cane sugar, having dextro-rotatory power, which by heating with an acid becomes "invert sugar" (a mixture of equal weights of dextrose and lævulose), and dextrose, or lævulose, or any mixture of them, or any other body not liable to have its rotatory power affected by heating with acids. Then the amount of *change* of rotatory power will be a measure of the cane sugar present in the original solution. If, for example, we had a mixture of 90 parts of cane sugar and 10 parts of dextrose, we should find on examining it as previously described, say with a Soleil-Duboscq polarimeter, that the direct reading gave 97·3 per cent. of sugar instead of 90, because the dextrose likewise rotated the ray to the right 7°·3 of the scale. On inversion the reading would be —25°·5, supposing the observation to be made at 15° C. The change produced by heating with acid was here from 97°·3 on the right to 25°·5 on the left, or a total of 122°·8. Now, 100 parts of pure cane sugar so treated give a change of 136°·5 at this temperature, and $\frac{122{\cdot}8 \times 100}{136{\cdot}5} = 90°$, the actual percentage of sugar present. As the left-handed rotatory power of "invert sugar" decreases rapidly with the temperature (about $\frac{1}{2}°$ of Soleil's scale, for each 1° C.), it is necessary to take exact account of the temperature at which the reading is made, and then to refer to Clerget's table, which will be found in most French and German works on the manufacture of beet sugar.

Estimation of Glucose.—The only method for estimating glucose in presence of cane sugar which seems to be sufficiently accurate for use is that commonly known as Fehling's, the best way of working which is found by the writer to be this:—Use the solution of sugar employed for polarizing, *after removing all lead from the solution*, and diluting to such an extent that the liquid does not contain more than 0·5 per cent. of the glucose. To remove the lead, measure off such a quantity of the liquid used for polarizing as experience shows will contain not more than 0·5 gram. or less than 0·2 gram. glucose; put it in a 100 c.c. flask, add solution of sulphurous acid till all lead is precipitated (if lead remains in solution, the results will come out much too low), add a little washed alumina, fill up to the mark with water, and filter. Fill the burette with this solution. Measure off with a pipette 5 or 10 c.c. of the "copper solution" into a test tube, $1\frac{1}{4}$ to $1\frac{1}{2}$ inch wide, and slightly blown out at the bottom, so that it shall be less liable to crack; dilute with about 3 volumes of water; put in a few fragments of clay pipe-stem to prevent bumping, and heat to boiling. Run in the sugar solution from the burette, 2 c.c. at a time, boiling up between each addition, till the blue colour has nearly disappeared; then more slowly, till on allowing the red cuprous oxide to settle, the liquid above seems colourless, or very faintly inclined to yellow, when the tube is held opposite a white surface (a distant white-washed wall is best). Worked thus the method gives very constant and accurate results, providing the copper solution is sound and the whole operation is *quickly* finished. As cane sugar likewise reduces the copper solution when long boiled with it, this last condition is obviously important.

As 0·5 gram. glucose (either dextrose or lævulose) will reduce the copper contained in 100 c.c. of the Fehling's solution, and as the above experiment gives the weight of the material containing 0·05 gram. glucose, the method of calculating the percentage of glucose is plain.*

Estimation of Water.—Weigh off 5 grams. of the sample (if it be a granular sugar) into a flat-bottomed platinum pan of good size (say with 3 square inches of bottom), spread it about evenly, and set it in an air-bath, heated to about 60° C. (140° Fahr.) in the case of cane sugars, or to 100° C. (212° Fahr.) in the case of "beets," and weigh at intervals of two hours till the weight is constant. The loss calculate as water. Twelve hours will be required for low "canes."

The estimation of water in low syrups—treacle, beet and cane juice, &c.—presents practical difficulties, owing to a skin forming over the surface, which prevents further drying at any moderate temperature. It is best therefore to proceed in one of the two following ways:—Weigh off 5 grams. of the sample, dissolve in water, and make up to 100 c.c. Of this solution take 10 c.c., and pour it over about 10 to 15 grams. of clean silver sand, which has been ignited and tared in a flat platinum dish; dry off at a temperature not exceeding 60° C. (140° Fahr.) till the whole ceases to lose weight on further heating. A small quantity being spread over a large surface dries readily.

The drying takes place with very great readiness, and at a lower temperature, if the pan be heated in a pretty good air-pump vacuum. For this purpose a convenient and cheap arrangement consists of a wide glass tube, run through an outer metal case which will hold water, and communicating at one end with a chloride of calcium tube and an air-pump, and which can be closed by a good rubber plug at the other. The pans here require to be long and narrow. In this apparatus the drying of half a gram. of syrup may be finished in a few hours.

Estimation of Ash.—Take the same or a similar portion of sugar; moisten it all over with the least possible quantity of water, and then with pure concentrated oil of vitriol; heat gently till the frothing has ceased, and the mass has become converted into a black cinder; and then introduce it into a muffle heated to very low redness (four ordinary Bunsen gas burners will heat a good-sized muffle to full redness, if the latter is so set in bricks that there is only about half an inch space between the two). When the carbon is about half burnt away, take out the pan and moisten its contents a second time

* The original statement of Fehling that the molecule glucose will reduce ten equivalents of cupric oxide, has been followed in the text; but the writer's own experience is that when the process of analysis is worked in the way described, the quantity of glucose required to fully reduce the copper oxide is two per cent. greater than there assumed.

with the sulphuric acid, and return to the muffle. Let it remain at a low heat till the ash is quite white, then raise the heat to full redness for ten minutes, withdraw, cool, and weigh. From the weight of sulphates so obtained deduct one-tenth, * and call the balance "ash."

On adding together the sugar, glucose, ash, and water found as above, it will be found that the total is something short of 100—usually to the extent of one and a half times to twice the weight of the ash; this difference is called "unknown" or "organic matter." As examples of such results, we may take the following analyses of low cane and beet sugars:—

Beet Sugar.		Cane Sugar.	
Sugar,	89·15	Sugar,	88·2
Glucose,	—	Glucose,	5·85
Ash,	2·63	Ash,	·90
Water,	4·26	Water,	3·98
Unknown,	3·96	Unknown,	1·07
	100·00		100·00

In the absence of a polariscope, or in cases where the quantity of sugar at command is too small to estimate by the use of that instrument, it may be necessary to determine the cane sugar present as well as the glucose by the use of Fehling's solution. For this purpose take a quantity of the material which contains about 10 grams. of sugar, clarify it as for polarization, *taking care to leave no lead in solution;* make it up to 1000 c.c. Estimate the glucose in one portion diluted with its own bulk of water; then take 50 c.c., add 5 c.c. hydrochloric acid, heat to 70° C. for five minutes. cool, nearly neutralize with sodium carbonate, make up to 100 c.c., and again determine the glucose. The difference in the glucose found in the two experiments is the glucose formed by the *inversion* of the cane sugar present. Each 0·05 gram. glucose so found = 0·0475 gram. cane sugar originally present in the portion used to decompose the 10 c.c. Fehling's solution. Of course material equal to about 1 gram. sugar can be made up to 100 c.c., as above, instead of 10 to 1000; the latter is recommended, to diminish the influence of errors of sampling. Some chemists estimate glucose gravimetrically instead of volumetrically—*i.e.*, they weigh the cuprous oxide precipitated from an excess of Fehling's solution by a known portion of the material under examination, after converting it into cupric oxide by ignition, and from this weight calculate the quantity of glucose; 397·5 parts of oxide obtained correspond to 180 parts of glucose, or 171 parts of cane, approximately; but the quantity of copper salt reduced by a given weight of glucose varies so much with the dilution, the alkalinity, the excess of copper salt present, and with the speed of the operations, that the method is only really applicable to the determination of comparatively small quantities.

Valuation of Sugars from the Analysis.—Raw or refined sugars fit for direct consumption are valued in an arbitrary manner, according to their appearance, colour, grain, &c., quite irrespective of their composition. Refiners value "sugars" mainly according to their estimate of the probable yield of pure dry sugar when submitted to refining. For market purposes the so-called French system is adopted. From the sugar found by the polariscope is deducted five times the weight of the ash, because it is assumed that the saline matters, represented by 1 part of ash, render 5 parts of sugar uncrystallizable; and from the remainder is deducted the weight of the glucose, because it is assumed that that body prevents the crystallization of its own weight of sugar, and the final result is taken as the "refining value" (*rendement*) of the given raw sugar.

A beet sugar giving in this way a refining value of 88 per cent. is taken as a standard of value, and other sugars are sold at so much a degree more or less. The above method rests on so many assumptions, which are all more or less demonstrably false, that no one can seriously suppose that the results represent anything more than a very rough approximation to the truth.

Scheibler, by improving the working details of a method proposed by Payen, determines the quantity of sugar *already crystallized* in a sample of raw; and assuming, as is generally true, that all the sugar is crystallized that can be—in other words, that any sugar which is still in solution in the syrup adhering to the grains is associated with so much other matter that it is not recoverable—takes the quantity so found as the true refining value, because it is presumable that what has been crystallized once may be crystallized again. The method is based on the fact that alcohol already saturated with sugar is capable of dissolving molasses, though incapable of taking up more sugar. He prepares three liquors by saturating alcohol of 85 per cent. (No. 1), 92 per cent. (No. 2), and 96 per cent. (No. 3) respectively with sugar, by long-continued shaking with the finely-powdered material at ordinary temperatures. The 85 per cent. spirit has about 5 per cent. of ordinary acetic acid added to it before saturation.

These liquors are preserved in bottles, coated on the inside with a crust of sugar; or, as the writer finds better, in large bottles quite filled with ordinary loaf sugar, free from dust, broken as it is for the table. This is to maintain a constant state of saturation, whatever the changes of temperature may be; but spirit which is nearly saturated with sugar dissolves the rest required with such slowness, that the maintenance of a nearly constant temperature is of great importance.

He weighs off the normal weight of sugar required for the polariscope in use; puts it into a tube like a test-tube, of about 8 inches by three-quarters, with a bit of quill tube fused into the bottom, and having a filter of thick felt or cotton-wool at the point of contraction. The narrow tube is attached by india-rubber, furnished with a compression cock, to a bottle in which a partial vacuum can be created.

* A continental practice, which is wildly supposed to reduce the sulphated ash to the same weight as the plain carbonated ash. As the operations of the trade are based on the weight of ash so found, it is necessary to adhere to the custom.

Liquor No. 1 is then poured into the tube, * and allowed to soak through the sugar slowly till it runs away into the vacuum bottle colourless, or very nearly so. Then this liquor is just sucked out, and the sugar left is rinsed successively by No. 2, No. 3, and finally by absolute alcohol. By sucking dry warm air through the tube the sugar can be speedily dried, and then weighed; but it is much quicker and better to transfer it to a 100 c.c. flask, dissolve, clarify, and "polarize" it. The results are very constant if no great variations of temperature have occurred since the liquors were saturated, and if the sugar under examination has been well air-dried for some time before being washed. Though constant and reliable for good "beet" sugars and nearly all "canes," the results are altogether fallacious when obtained from low beets (second and third runnings), because in these, which have been crystallized very slowly, many of the salts are in combination with sugar in the form of crystallized compounds which are not dissolved by the liquors, but which, when dissolved in water in the process of refining, cannot be recrystallized in the time at command. Moreover, the method assumes that all the sugar which is in solution in the adhering molasses will pass into the final residue of molasses, or that all the impurities which interfere with the crystallization of the sugar will remain intact and undiminished, although it is certain that some of the worst of them (such as the gummy bodies) will be removed from the solution by the animal charcoal or other purifying substances or processes.

STAMMER, a very careful chemist and practical sugar maker, states that according to his experience the actual out-turn in refining beet sugar differs but very little from that calculated on the French system. WEINRICH, WEILER, and SCHULTZ—the latter from the experimental work of years in a refinery—come to the conclusion that in practice the out-turn in refined sugar equals the total sugar, less the total solid impurities (soluble) × 2. This applies to beet sugars only.

Strength of Liquors.—Among the constantly recurring operations of a sugar factory or refinery, none comes round so often as the making a rough determination of the strength of syrups, &c., by help of some sort of specific-gravity float. The almost universally used BEAUMÉ'S float is graduated thus:—The point to which it sinks in pure water is marked, and then that in which it stands when immersed in a solution of 15 parts of pure, dry, common salt in 85 parts of water. The space between is divided into 15 equal parts or degrees, and the scale so made continued on to thirty or more similar and equal divisions. This scale is thus purely arbitrary, and needs the use of a table to reduce its readings to percentages of sugar—or rather of *apparent sugar* — since very few sugar liquors so tested consist of pure sugar and water, and the other soluble solids likewise raise the specific gravity. In the absence of a table it is sufficient to multiply the degree BEAUMÉ by 1·8, in order to find very nearly the apparent sugar contents.

Degree, Beaumé.	Per cent. apparent. Sugar by Weight.	Specific Gravity of the Solution.	Degree, Beaumé.	Per cent. apparent. Sugar by Weight.	Specific Gravity of the Solution.
0	0·00	1·0000	26	47·73	1·2203
0·5	0·90	·0035	26·5	48·68	·2255
1	1·80	·0070	27	49·63	·2308
1·5	2·69	·0105	27·5	50·59	·2361
2	3·59	·0141	28	51·55	·2414
2·5	4·49	·0177	28·5	52·51	·2468
3	5·39	·0213	29	53·47	·2522
3·5	6·29	·0249	29·5	54·44	·2576
4	7·19	·0286	30	55 47	·2632
4·5	8·09	·0323	30·5	56·37	·2687
5	9·00	·0360	31	57 34	·2743
5·5	9·90	·0397	31·5	58·32	·2800
6	10·80	·0435	32	59·29	·2857
6·5	11·70	·0473	32·5	60·27	·2915
7	12·61	·0511	33	61·25	·2973
7·5	13·51	·0549	33·5	62·23	·3032
8	14·42	·0588	34	63·22	·3091
8·5	15·32	·0627	34·5	64·21	·3151
9	16 23	·0667	35	65·20	1·3211
9·5	17·14	·0706	35·5	66·19	·3272
10	18·05	·0746	36	67·19	·3333
10·5	18·96	·0787	36·5	68·19	·3395
11	19·87	·0827	37	69·19	·3458
11·5	20·78	·0868	37·5	70·20	·3521
12	21·69	·0900	38	71·20	·3585
12·5	22·60	·0951	38·5	72·22	·3649
13	23·52	·0992	39	73·23	·3714
13·5	24·43	·1034	39·5	74·25	·3780
14	25·35	·1077	40	75·27	·3846
14·5	26 27	·1120	40·5	76·29	·3913
15	27·19	·1163	41	77·32	·3981
15·5	28·10	·1206	41·5	78·35	·4049
16	29·03	·1250	42	79·39	·4118
16·5	29·95	·1294	42·5	80·43	·4187
17	30·87	·1339	43	81·47	·4267
17·5	31·79	·1383	43·5	82·51	·4328
18	32·72	·1429	44	83 56	·4400
18·5	33·65	·1474	44·5	84·62	·4472
19	34·58	·1520	45	85·68	·4545
19·5	35·50	·1566	45·5	86·74	·4619
20	36·44	·1613	46	87·81	·4694
20·5	37·37	·1660	46·5	88·88	·4769
21	38·30	·1707	47	89·96	·4845
21·5	39·24	·1755	47·5	91·03	·4922
22	40·17	·1803	48	92·12	·5000
22·5	41·11	·1852	48·5	93·21	·5079
23	42·05	·1901	49	94·30	·5158
23·5	42·99	·1950	49·5	95.40	·5238
24	43·94	·2000	50	96·51	·5319
24·5	44·88	·2050	50·5	97·62	·5401
25	45·83	·2101	51	98·73	·5484
25·5	46·78	·2152	51·5	99·85	·5568

A very convenient and instructive method of comparing one juice or one syrup with another is to determine in each case, first, the specific gravity (and hence the quantity of soluble solids, supposing they all had the same density as sugar in solution), and then the real quantity of sugar present. The percentage of sugar contained in 100 parts *apparent solids* may be called the "apparent purity coefficient" of that juice or syrup, and serves better than any other number as a means of comparison of one with another. Of course the real "total solids" may be determined, and the real purity coefficients found;

* SCHEIBLER himself first pours absolute alcohol into the sugar, and allows it to stand some time to take up the water of the molasses, to prevent the dilution of solution No. 1 to such an extent that it could dissolve any of the crystallized sugar. It is, however, in every way better to suck dry, and if possible, warm air through the tube and its contents till the greater part of the water is removed. In this way one avoids the danger of precipitating more sugar from the molasses (by the alcohol), and so obtaining results too high.

but in practice this is beset with great difficulties, and the *apparent purity* coefficient is a more practically useful datum.

Beet-sugar Manufacture.—Although the manufacture of sugar from the beet (*Beta vulgaris*) is not practised in England, and to but a slight extent in any of her colonies, the methods of extracting the juice and subsequently working it up to sugar have been so perfected by the application of the highest skill and science, that a knowledge of them cannot fail to afford some useful and pregnant hints to the makers of cane sugar. It therefore seems useful also to consider this branch of the production of raw sugar.

The "sugar beet" is an improved variety of the common white beet; the best varieties of it, such as the "White Silesian," the "Imperial," and "Vilmorin's Imperial," are characterized by having a root of moderate size (1½ to 2½ lbs.), a regular pear or spindle shape, without ramifications or secondary roots; a somewhat hard, compact, white substance; a small neck or shoulder, which appears very little above ground; and above all, a large percentage of sugar, and a small one of other soluble matters. The soil best suited to the growth of good sugar beet is a deep calcareous loam, free from any large number of loose stones, which have a tendency to make the roots fork, and themselves sometimes get so imbedded in the tissue that they escape removal during the cleansing, and then work ruin to the rasp. Though the soil described is the best, the beet is so accommodating that it will flourish in any soil of sufficient depth, if well drained and not too peaty. Nitrogenous manures, particularly nitrate of soda, in large quantities produce luxuriant growth, but unfortunately, at the same time, increase the proportion of soluble non-saccharine substances in the juice to such an extent as seriously to interfere with the subsequent extraction of the sugar. It is therefore advisable to manure the previous crop, say wheat, pretty heavily, and to give the beet itself nothing but "superphosphate."

In order to grow a paying crop of the small roots, which alone are of sufficiently good quality for the factory, it is found that the best method is to plant very close—at least twice as close as in the case of mangolds—then numbers make up for want of size. It must never be forgotten that large roots are bad roots, with watery, salt juice. According to some experiments made a few years ago in England, the crop varied in different localities from 18 to 30 tons to the acre, and the roots contained from 8 to 16 per cent. of sugar. The present writer carefully examined the roots grown in different places in the eastern and southern counties, and found that, in regard to richness in sugar and purity of juice, many were far superior to those grown and worked in France, and fully equal to the best of the German. There is therefore nothing in the soil or climate of this country to prevent this useful industry finding a place among us. For details of the method of culture and preservation of the root the reader is referred to Stammer's "Traité Complet de la Fabrication du Sucre." The quantity of juice contained in beet-root varies but little from the standard of 94 per cent.; but the percentage of sugar in the juice, and the proportion of soluble foreign bodies associated with that sugar, are very variable, as shown by the following analyses, quoted from the above celebrated authority, as far as the French and German roots are concerned:—

	Weight of the Roots (each) in grammes.	Apparent Sugar from specific gravity (Per cent of Balling).	Per cent of Sugar in Juice, shown by Polarization.	Per cent. of Sugar on total apparent solids (coefficient of purity.*
German roots.	350	18·1	14·9	82·3
	760	15·7	12·9	82·4
	640	16·0	12·8	79·7
	532	19·	17·1	90·0
	700	16·	13·6	85·0
French roots.	2500	13·3	10·6	79·7
	1876	14·2	11·6	81·7
	1375	10·1	4·6	45·5
	523	13·2	12·0	90·9
English roots.	682	18·5	15·5	85·4
	961	17·0	14·0	86·0
	680	19·0	15·36	84·4
	650	15·8	12·6	83·2
	1147	15·3	12·0	82·1

When the purity coefficient falls below 75 per cent. the roots are too impure to work with profit.

When the roots are delivered at the factory, the first operation is to wash them thoroughly, to remove dirt and stones. This washing is effected by the aid of mechanical washers, consisting of a drum or cylinder of iron laths revolving horizontally in a trough of water about half its diameter. The washed roots are then taken up one by one in the hand, examined to see if any stones still adhere, and are trimmed by a knife, by having the neck or that portion which grew out of the ground removed, as well as any small or secondary roots.

There are two principal methods for extracting the juice from the root: the one based on rasping the root to a fine pulp and expressing the juice by pressure, and the other on slicing it and extracting the sugar by systematic soaking in water. The first, which is almost exclusively used in France, is certainly the simplest, and on the whole the best, when it is not of importance to extract the last trace of sugar. As, owing to the absence of all duty on sugar, this would be the case in England, it is probable that any one erecting a factory there would find it advantageous to extract as much juice from the rasped roots as he conveniently could in a rapid and economical manner, and to utilize what remained in the pressed pulp to feed cattle.

The rasp used to reduce the roots to pulp consists of a large number of small straight saw blades, set along the face of a drum at about a quarter of an inch apart. This armed drum is mounted on a horizontal axis, and surrounded with a case which approaches the drum closely at its sides, and which is expanded into a hopper at its upper part. The drum is caused to rotate at a velocity of 600 to 1000

* By *apparent* solids is meant that quantity of soluble bodies which is shown as sugar by the areometer, *i.e.*, the per cent. of sugar shown by the specific gravity float, or the per cent. balling, as given in the second column of the table.

turns a minute, while the cleansed roots are fed into the hopper and are pressed up to the rasping face, either by their own weight or by a mechanical arrangement which is not necessary to describe. At the same time a stream of water, equal in all to about 50 per cent. of the weight of the roots rasped, is allowed to run on the face of the rasp, to assist in keeping the teeth clear, and to render the pulp more fluid and more readily pressed. The pulp being obtained, the juice is extracted from it either by pressing in woollen cloths, by means of an ordinary hydraulic press; or by feeding it into centrifugal machines, and when the greater part of the juice has been spun out, giving a good washing with a measured dose of water; or lastly, by passing the pulp through one of the so-called continuous presses.

In an article of this kind space fails to give a usefully-detailed description of the plant required for each, or, indeed, any of these methods; it must therefore suffice to say that the continuous presses consist essentially of three or more rollers, somewhat similar to an ordinary cane-crushing mill, between which the pulp is fed by being carried on an endless band of cloth. In some of the many forms of the machine one or more of the rollers are perforated, to facilitate the escape of the juice before it can be re-absorbed by the pulp when relieved of the pressure of the rollers. These continuous presses extract less of the juice than the hydraulic presses by about 3 to 5 per cent.; but this is not lost where cattle are fed on the pulp, and the labour of many hands is saved. By re-rasping the pulp with further addition of water, and passing it anew through a second press, a large proportion of the remaining juice is extracted in a diluted state, and can be used in place of pure water on the rasp with fresh roots.

In this last case the yield of juice is almost equal to that obtained by the hydraulic presses, or about 80 to 83 per cent. out of the 94 per cent. which the roots contain. The last and perhaps the best of the continuous presses is that of MM. Manuel and Socin, which, with the extreme dimensions of 7 by 13 feet, will press the pulp from 50 tons of roots per day of twenty-four hours.

The second principal method of extraction—the so-called diffusion process—is employed very largely in Austria and Russia, where it is of the utmost importance to the manufacturer to extract the greatest possible quantity of sugar from the roots, because he pays duty on the estimated weight of the latter, and obtains from his Government such a drawback on the export of the raw sugar that each pound of sugar which he wins is worth to him nearly twice its intrinsic value.

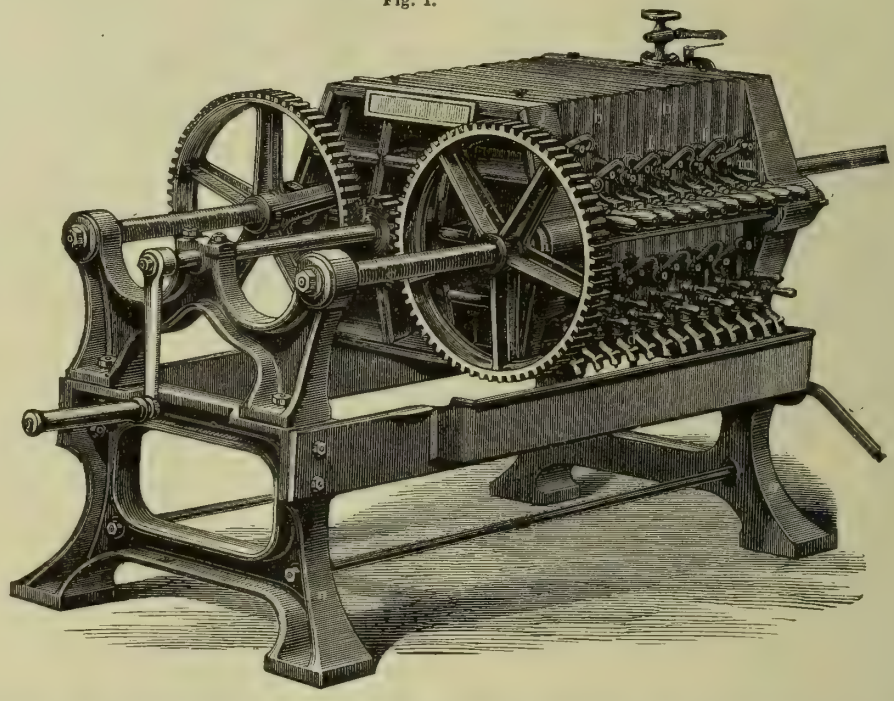
The roots are sliced up into strips, about half an inch broad and one-quarter thick by 2 to 4 inches long, by help of a machine, which may be described as an improved turnip slicer. The strips are then fed into a series of iron cylinders, about 6 feet high and 4 feet diameter, furnished with a false bottom and two man-holes—one just over the false bottom and one at the top. These diffusers are so connected together by pipes and valves, that the fluid contents of any one of the series of six or more can be forced on into any other by simply driving more liquid into it. Suppose all to be filled with sliced roots except the last, and that cold (or slightly warm) water is made to pass into the top of the first, and after filling it, out of the bottom to the top of the second, and so on to the end of the series. During the stay of the first portion of water on the sliced root in the first diffuser it would receive a certain quantity of sugar by exosmose from the cells—indeed, if it stood long enough, the proportion of sugar to water would be the same inside and outside the walls of those cells. This weak solution of sugar would pass on to a fresh lot of root, and become stronger; and so on in each succeeding vessel. But the first diffuser would all this time be receiving fresh quantities of water, so that by the time the sugary liquid began to run from the last of the series, the whole, or very nearly the whole, of the sugar would have been soaked out of the strips in the first vessel. When this point has been reached, the first vessel is disconnected from the series, to be emptied and refilled with fresh-sliced roots; the second vessel then becomes the first to receive the fresh water; while the spare vessel, which was not used at first, is brought into work at the end of the series. In this way the freshest and least-exhausted roots are always soaked in a solution of sugar only a little less concentrated than their own juice, while those which are nearly freed from sugar find themselves in fresh water.

The extraction of juice by this method is very perfect, and the product is comparatively pure, because the albuminous and gummy bodies associated with sugar in the juice of the beet are not capable of diffusing with any rapidity through the membranous walls of the plant cells in which they are confined. In this process the quantity of water used is about two and a half times the weight of the roots; but as a very large proportion of this water remains in the exhausted slices, the dilution of the juice is only about equal to 50 per cent. The loss of sugar by imperfect extraction rarely exceeds 0·5 per cent. of the weight of the roots.

Defecation.—The juice having been obtained by one or other of the above methods, is treated with an excess of lime, which ordinarily amounts to one-half to three-quarters per cent. of the weight of the roots operated on. This lime is added to the juice, heated to about 85° C. (185° Fahr.) in a copper pan, provided with a steam jacket. The admission of steam to the jacket is continued till the liquid is just on the boil, and beginning to break through the crust of scum formed on its surface. The visible effect of this treatment is to change the dark, blackish-green juice to a clear light yellow. The real purifying effect is small as regards the separation of weighable quantities of foreign bodies, but important as removing some of the most prejudicial, and so altering others that they are either rendered less noxious or more easily removed at subsequent stages of the manufacture.

The clear, highly-alkaline juice is drawn off from below the scum, and while still hot submitted to the action of a stream of carbonic acid gas, obtained either from the burning of coke or charcoal, or drawn from the top of a special lime kiln. The carbonic acid unites with the excess of lime left in the defecated liquor, forming insoluble carbonate of lime, which, in precipitating, carries down with it some of the organic impurities of the juice as a sort of "lake." This "carbonation" is pushed so far as still to leave the juice slightly but distinctly alkaline. The right point is marked by the ready separation of the carbonate of lime in granular flocks; or in certain cases, is found by means of a very weak solution of an iron salt, from which a juice which is still alkaline precipitates an oxide. The turbid liquid is then allowed to settle for some time, and the clear portion run off from the sediment, and either again limed and again carbonated, or passed straight to the charcoal filters after being reheated. The sediment of carbonate of lime, together with the juice mixed with it, is passed through filter presses, and the clear filtrate added to the rest of the liquid. At the present time the defecation and carbonation are combined in one operation (*procédé Jelineck*, or *carbonatation troublé*) in a very large number of factories. Lime in considerable quantity (1·5 to 2·5 per cent. on the roots) is added to the slightly-warmed juice, and the stream of carbonic acid gas turned on, while the temperature is allowed to rise at such a rate that a temperature of about 93° C. (200° Fahr.) is attained, at the same time that the elimination of the excess of lime becomes sufficiently complete. The whole mass of turbid liquid so

Fig. 1.



produced is then forced through filter presses. It is found that the total purifying effect of defecation and carbonation (saturation) is equal to the removal of about 40 per cent. of the soluble impurities originally present in the juice; and as the alkaline salts are not at all diminished, this purification must mainly consist of the removal of the albuminous and gummy bodies.

The filter presses alluded to above have many forms, but all consist essentially of a series of perforated metal plates, covered with wire-gauze and cloth, and so arranged between movable frames of wood or iron that the space between each two cloth-covered surfaces can be filled with the liquid to be filtered under any desired pressure, while the clear liquid escapes on the other side, and is conducted into a channel communicating with a reservoir. Fig. 1 represents the arrangement of this filter press. The lime scums from the purification of beet juice are separated with great ease by this apparatus in the form of cakes, which only need to be again broken up with water and dosed with carbonic acid, and passed again into a fresh filter press, to be almost entirely freed from adhering sugar. It is not too much to say, that without this most valuable piece of apparatus the beet-root sugar industry would never have attained its present perfection. The extreme convenience and rapidity of working which it exhibits in the beet factory have naturally induced repeated trials of it for the purpose of clarifying cane juice and the liquors of the refinery. These attempts have hitherto failed, the sliminess of cane juice and liquors from raw cane sugar causing the filtering surfaces to become rapidly

choked. Further trials are, however, being now made by Bowing, the patentee of a new form of the apparatus.

Charcoaling.—The thin defecated and carbonated juice, still containing a minute percentage of lime and all the potash and soda originally present, together with a considerable proportion of non-saccharine organic bodies, is then passed through a deep bed of animal charcoal. The cisterns of char filters are usually about 15 feet deep, and only about $2\frac{1}{2}$ to 3 feet in diameter, but have otherwise the form and disposition of parts common to those used in the refinery.

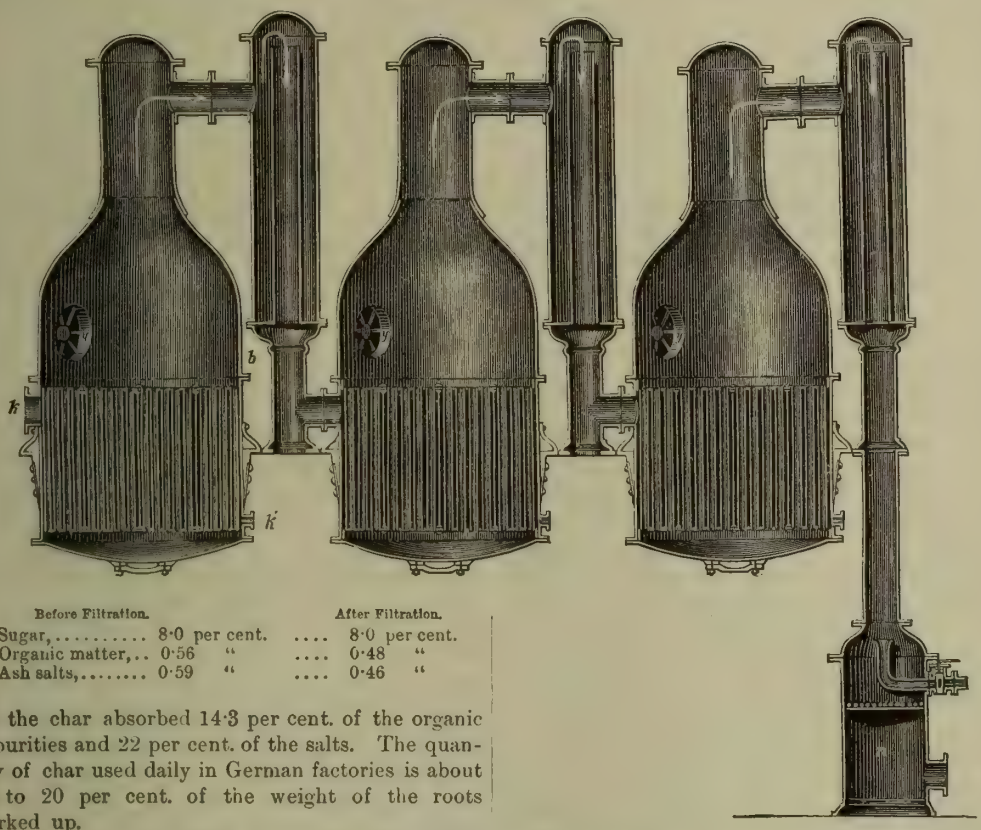
The char is used in grains or fragments nearly as large as small beans; and before the juice is allowed to flow into it, it is thoroughly steamed out, and is used hot. As such precautions are found in practice to be necessary for the beet juice, though not for the thick liquors of a refinery, it is worth while for those manufacturers of cane sugar who have met with difficulties in their attempts to employ animal charcoal, to take this hint from their rivals.

As an example of the amount of purification effected by char on the thin juice a determination by Rabe may be cited. The juice defecated and carbonated contained—

	Before Filtration.		After Filtration.	
Sugar,.....	8·0	per cent.	.... 8·0	per cent.
Organic matter,..	0·56	"	.... 0·48	"
Ash salts,.....	0·59	"	.... 0·46	"

Or the char absorbed 14·3 per cent. of the organic impurities and 22 per cent. of the salts. The quantity of char used daily in German factories is about 15 to 20 per cent. of the weight of the roots worked up.

Fig. 2.



First Concentration.—The charcoaled "thin juice" is next concentrated by evaporation to about 20° B. To effect this the so-called "double" or "triple effect" vacuum pan is employed. In this instrument the vapour (steam) rising from the boiling solution in one pan is made to pass into the worms or heating tubes of the next, and the vapour from the second into the worms, &c., of the third. In theory the number of pans so arranged, one after the other, might be largely increased with corresponding economy; but from various causes, such as loss of heat by radiation, &c., three are found to be as many as can advantageously be worked in this way. In Fig. 2 it will be seen that the worms of an ordinary vacuum pan are here replaced by a steam-chest, which is traversed by a large number of vertical tubes which are open at top and bottom to allow the boiling solution to circulate freely. The steam for boiling is introduced into the steam-chest so as to surround the outsides of the boiling tubes. In other modifications of the apparatus the bodies of the pans have a form similar to locomotive boilers, and, like them, are furnished with a large number of horizontal copper tubes, which in this case convey the heating steam. In whichever form it is used, a fairly good vacuum is maintained in the third pan (about a 25-inch vacuum), a less vacuum in the second, and none in the first. In consequence of this the liquid in the first pan boils at about 100° C., that in the second at about 15° C. lower, and that in the third at 20° C. lower still. In this way the necessary difference in *temperature* between the heating

surface and the liquid to be boiled is maintained. The steam from the boilers (or the exhaust steam from the engines) is admitted to the heating surface of the first pan only, at *k* in the apparatus shown; it should have a temperature of about 105° to 110° C. (= about 5 to 7 lbs. steam); this causes the thin juice to boil rapidly at about 100° C., giving off, of course, vapour of the same temperature. This cooler steam (which, however, contains nearly the same *quantity of heat*, sensible and latent together, as an equal weight of steam of higher temperature) passes into the heating chamber of the second pan, and is condensed into water, at say 85° C., which runs away through a special arrangement not necessary to describe. The vapour from the sugar liquor in the second pan passes into the steam chest of the third, and being there condensed by the colder liquid contained in the tubes, creates the partial vacuum required in the second pan. The vapour from the third pan is taken straight to a condenser and vacuum pump, such as are used with an ordinary vacuum pan. Space fails in which to consider scientifically the action of this valuable apparatus or its detailed construction. The thin juice, when it has submitted to a certain amount of concentration in the first pan, is passed on to the second, and then in turn to the third, where it is brought to about 20° to 25° B.

On leaving the third pan it is heated to nearly boiling point, and again passed through fresh charcoal filters, from which it proceeds to the vacuum pan to be boiled to grain. This second filtration is always made through freshly-reburnt char, which removes more of the impurities remaining after the first filtration. As an example of the purification effected, a determination by RABE may be quoted. A "thick juice," containing 47·5 per cent. sugar, 2·8 per cent. organic impurities, and 2·6 per cent. ash before filtration, showed after filtration 2·4 per cent. of organic impurities and 2·0 per cent. ash; or the char had absorbed 14·3 per cent. of the former and 23 per cent. of the latter. As the vacuum pan and its use is described elsewhere, it needs no special remarks here, except that owing to the often low quality of the juice operated on, and its alkalinity, the boiling is sometimes slow and difficult. MARGUERITE has found that the addition of a mineral acid, such as sulphuric or hydrochloric—in quality sufficient, not only to completely neutralize the free alkalies present, but to convert most of the salts of organic acids present into sulphates or chlorides—greatly facilitates the boiling, and gives a "green sugar" more easily and better cured in the centrifugals. Moreover, he found (and extensive practice on the large scale quite confirms the laboratory experiments) that at the temperature due to the decreased pressure in the vacuum pan, the liberated organic acids exert little or no inverting power on the sugar. It is worthy of note that though MARGUERITE was the first to publicly advocate the use of strong acids in this way, and to explain the safety of the process, the thing itself had been done extensively long before in Demerara.

The grained sugar, as it leaves the pan, is treated differently according as it is intended to make yellow refining sugar, white crystals, or low-quality loaf sugar. For details of these various treatments the reader is referred to special works. Supposing white crystals are to be made, as is most commonly the case in France, the *masse cuite* is allowed to cool somewhat in a shallow tank for three or four hours; and is then broken up in an agitator with some syrup, and fed into the centrifugal machines. When as much of the syrup is spun off as possible, the contents of the machine receive a dash of water, or of the thick juice in the state in which it goes to the vacuum pan; this removes more of the adhering mother liquor from the crystals, which are finally cleansed and dried by blowing steam into the basket of the machine by a suitable arrangement.

The syrup from this first crop of sugar is again boiled in the vacuum pan, but on account of its low quality, only to "string"—*i.e.*, to such a degree of concentration that a few drops placed between the finger and thumb will draw out to a thread two or three inches long before breaking. It is then allowed to stand in iron tanks, at a temperature of about 40° C., for ten days or a fortnight to crystallize. The grained mass is then dug out, broken up with more syrup, and spun, when it furnishes a crop of second-running sugar. The syrup is again concentrated to "string," and allowed to stand for five to eight months in large underground iron tanks or brick cisterns, when a third crop of sugar is obtained. The syrup from this last constitutes beet molasses, which have hitherto found their way to the distillery, but are now being treated as described further on.

The first crop of sugar being crystallized rapidly at a comparatively high temperature, consists of almost pure sugar crystals, coated more or less with their mother liquor, which, being removed as described, leaves a "sugar" rarely containing more than one-half per cent. of impurity, including moisture. The crystals of the second crop, and still more those of the third, having formed slowly in presence of large quantities of salts of the alkalies, always contain a considerable quantity of those bodies united with the sugar, as explained under "Compounds of Sugar;" consequently there is afforded a ready means of distinguishing between first and second or third running beet sugars, or of detecting any considerable fraudulent admixture of these latter with the former, by first removing all adhering syrup from the grains of the sugar, by washing with acidified spirit of about 85 per cent. (say SCHEIBLER'S liquid, No. 1), and then ashing a known weight of the residue with sulphuric acid, as usual. A pure first-running sugar will always give less than 0·2 per cent. of soluble ash, while a third-running sugar may give as much as 2 to 5 per cent.

As examples of the composition of yellow German beet sugars and beet molasses, the following analyses are given. It will of course be understood that there is very great variation in different samples, according to their origin, &c. :—

	1st Running.	2nd Running.	3rd Running.	Molasses.
Sugar,	95·1	93·	92 1	50·9
Glucose,	—	—	—	1·1
Ash,	1·41	2·61	2·76	12·9
Water,	1·44	2·72	2·90	19·0
Organic impurity,	2·05	1·67	2·24	16·1

Elution.—One of the most promising and important improvements in the manufacture of beet sugar that has been made for some time is the so-called elution process of Scheibler, as improved and rendered practical by Seyferth and others. The object of this process is to recover the sugar contained in the stinking, black, almost unsaleable molasses of the beet-sugar factory. Good ground lime is added, little by little, to the undiluted molasses contained in a vessel provided with stirring gear, in the proportion of 84 parts pure lime for each 171 parts sugar (3 molecules lime to 1 of sugar). Combination of the sugar and lime takes place, and heat is evolved. The granular mass which ultimately results from this operation is then extracted with alcohol of 35 volume per cent., which dissolves the free alkalies and salt, and most of the non-saccharine organic bodies, leaving tribasic sugar-lime in a tolerable state of purity. The alcohol used can be recovered with but little loss by distillation, and the sugar can be (and is) obtained from the sugar-lime either by directly saturating it with carbonic acid, or better, by using it in place of fresh lime for defecating fresh juice. In practice about four-fifths of the sugar of the molasses is now won in this manner.

Another method of winning a part of the sugar of molasses: Dubrunfaut's "Osmose process" is at present attracting much attention in Austria and Russia, where, as before explained, each pound of sugar recovered has a double value. It depends on the removal of part of the salts by the help of their superior power of diffusion through organic membranes. In principle the molasses are confined on one side of a sheet of parchment paper, and clean water on the other. Salts and sugar pass through to the water, and water passes back to the molasses; but the salts diffuse more quickly than the sugar, so that, at the end of a certain period, what remains on the molasses side of the parchment is a diluted solution of molasses, containing a smaller quantity of salt in proportion to the sugar than originally. The removal of this salt does, in fact, allow of a fresh quantity of sugar to be extracted by crystallization, which is very direct proof that salts do interfere with crystallization of sugar, which has been denied. The proportion of salts to sugar in cane juice, and sugars made from it, is too small to allow of their profitable removal by this process; and the glucose, which is the characteristic impurity of sugars from the cane, diffuses far more slowly than cane sugar itself.

Manufacture of Sugar from the Cane.—1. *Cultivation of the Cane.*—The sugar cane—*Arundo saccharifera*—is an indigenous plant of the gramineous family. Cultivators distinguish three great varieties—the Creole, the Batavian, and the Otaheite cane. The first is indigenous to India; but it has been transplanted to other soils, such as those of Sicily, the Canaries, the Antilles, South America, and the West Indies. It is known by its thin, very knotty stem, and green leaves. The Batavian cane is a native of Java, but is met with at present in some of the sugar plantations of the New World and the West Indies; it is covered with purple stripes, and has a heavy foliage. The Otaheite variety is spread over the West Indies and South America, and is esteemed by far the richer and more productive of the several species. There are besides, the purple-banded and the purple Otaheitan and the ribbon cane. The Bourbon is said to be the same as the Otaheite cane of Singapore.

The sugar cane in a state of maturity is usually from 6 to 15 feet in length, and from 1½ to 2 inches in diameter. It is jointed, and the distance of the joints from one another is from 3 to 7 inches. These joints correspond to the extremities of hexagonal cells, of which the intermediate portions of the stem are composed, and which are in the living state of the plant filled with a solution of sugar. The exterior of the cane is smooth, hard, and cylindrical, and is covered with a coating containing a large quantity of silica. Germination occurs at the joints, and takes place at the opposite sides of alternate joints.

The sugar cane grows from pieces or slips of itself containing germs, and these develop rootlets at the joints, which draw sustenance to the young shoot as it increases. In the course of time the buds in the radicle, or root joints, of the first cane throw out roots, and form a radicle for a second stem; and in this way it happens, under favourable circumstances, that several canes are produced from the parent stock for a period of about six years, sometimes even for twenty years. From the first and second year, however, the canes diminish in the length of joint and circumference, and so the quantity of juice decreases; but it is alleged that the juice is much richer than when younger, and also produces a finer sugar. A common mode of obtaining successive crops is as follows:—When an old cane has been cut for its sugar, the incision is made some inches below the ground, and the stump covered with mould. In about twelve months' time the offshoots from the original cane are ready for transplanting. In planting these slips or *ratoons* the system of wide planting is gradully superseding the old close planting. In addition to the advantage which the former kind offers in allowing the use of the horse-hoe for weeding, the great length of the root of the sugar cane, which often extends laterally to a distance of 6 and vertically to a depth of 2 feet, makes wide planting imperative, when rapidity of growth, as determined by quick absorption, is required. The cane holes are advantageously formed 5 feet from one another, in rows which are also 5 feet apart; or, as some say, even 8 feet.

Of late years the system of cultivation of the sugar cane has attracted considerable attention, as well in regard to the preparation of the soil as to the manner of planting. Formerly the custom of

preparing the land by manual labour was followed; it is sometimes so still, and the consequence of not having the soil sufficiently disintegrated to the proper depth required by the plant made itself apparent in the defective harvests of the plantations which followed; besides, by the practice of utilizing for fuel the *megass* or expressed cane, called *cane straw* and *cane trash*, instead of returning it to the land, the latter was rendered deficient in humus, and therefore not suited to retain the proper quantity of moisture, which in the warm climates of its growth the cane absolutely requires for its proper development. And although the ashes of the refuse might be consigned to the soil, yet this, instead of improving, rather defeated the objects which the cultivators had in view, as by the use of too much mineral matters as a manure, the sugar secreted by the plant was rendered uncrystallizable, and so, in a comparative sense, lost to the planter. An excess of soluble salts should always be guarded against in the cultivation of the sugar plant; but the fertilizer should be rich in humus and nitrogenous constituents, as the consumption of both these classes of bodies by the plant is greater in a much larger proportion than of mineral fertilizing matters. The knowledge of these facts has led to the desire of employing such matters as blood, decomposed flesh, rotten fish, wool refuse, and the like, for manure in the sugar plantations.

The frequent droughts which occur in the countries adapted to the cultivation of the sugar plant, render the artificial prevention of the too rapid evaporation of the water, which would be very injurious to the freshly-planted ratoons, of the highest importance. The great bulk and solidity, and the richness in mineral constituents of the stem of the sugar cane, would cause a rapid impoverishment of the soil, were not some adequate return made to it. Both purposes are effected by surrounding the stems of the newly-planted ratoons with the *megass*, or cane from which the sugar has been extracted.

Canes require a soil well drained, but still rich and moist. Land with much saline matter is frequently found to prevent the canes ripening; they remain green and watery.

One variety greatly in cultivation in Jamaica came from Otaheite. When this cane is well cultivated, and in favourable soil, it rises in the first year to 12 or 14 feet in height, being 6 inches in circumference, and having joints 6 inches apart. No field, however, will give an average so high as this. It sometimes attains maturity in ten months. Its foliage is of a pale green; leaves broad and much drooping, and flowering or arrowing in a manner graceful and ornamental. It requires a rich soil. The *yellow-violet* may be put in poorer soil. It gives a fine sugar, but not so much as the Tahiti cane. It has a dark-green foliage. The *purple-violet* is from Java, and is 8 to 10 feet high, and 6 inches in circumference. On the joints of the cane there is a large amount of a resinous film, which sometimes completely shades the purple beneath. This resin is very hard and troublesome to grind. The cane itself is hardy, and is sometimes used in Jamaica as a border to other canes, defending them against the trespassing of cattle.

The large red cane of Assam is said to flower in eight months, and to give similar sugar to the Tahiti cane. In Bengal a large red cane is cultivated which gives excellent sugar. The China cane is said to be extremely hardy, standing both cold and drought, and, with abundant rain, giving out as many as thirty shoots. It resists the inroads of the white ants, which cannot penetrate its hard crust, whilst it is also safe against the teeth of the jackals. It requires, however, a stronger mill for grinding than the other varieties mentioned. Wray asserts that the Salangore cane is the finest in the Straits of Singapore, and perhaps in the world. He says that he has cut five from one stool, which were of a weight of from 17 to 25 lbs. They have been known to produce 7200 lbs. of undrained sugar per acre, equal to 5800 of dry sugar for shipping.

A dry, smooth, brittle skin, a heavy cane, a grey pith, approaching to brown, and a sweet glutinous juice, indicate the maturity of the cane. The canes should be cut so that the juice may not be diluted at a dry season. The canes are cut as close to the *stole* or root as possible, as well because the lower joints are found richer in sugar, as to give vigour to the ratoons which are to spring from the old stock; the tops, with one or two joints, if they be not sufficiently ripe, are cut off, and the canes tied in bundles and conveyed to the crushing mill. It is absolutely necessary that the cane be cut just before being expressed in the mills; for, if allowed to remain any length of time at the high temperature of the climate, the sugar ferments, and a considerable loss is consequently occasioned. The following tables are from Payen:—

OTAHEITE CANE AT MATURITY.

	Centesimally.
Water,	71·04
Sugar,	18·00
Cellulose, ligneous matter, pectin, and pectic acid,	9·56
Albumen and three other nitrogenous matters,	0·55
Cerosin, green matter, yellow colouring substance, substance capable of being dyed brown, and carmine, fatty matter, resins, essential oil, aromatic matter, and a deliquescent substance,	0·37
Insoluble salts 0·12; soluble 0·16; consisting of phosphates of lime and magnesia, alumina, sulphate and oxalate of lime, acetates, malate of lime, potassa, and soda, alkaline chlorides, and sulphates,	0·28
Silica,	0·20
	100·00

CANE ONLY AT A THIRD OF ITS DEVELOPMENT.

	Centesimally.
Water,	79·70
Sugar,	9·06
Cellulose and incrusted ligneous matter,	7·03
Albumen and three other nitrogenous substances.	1·17
Starch, cerosin, green matter, yellow colouring substance, and bodies colourable to brown and carmine,	1·09
Fatty, aromatic, and hygroscopic substances, essential oil, soluble and insoluble salts, alumina, and silica,	1·95
	100·00

The amount of water in the sugar-cane increases, according to CASASECA, towards the top; the greatest amount of sugar is found in the lower third of the cane, but much less in the upper part; the centre third contains about an average of the whole. The water even of the joints increases on rising.

The following additional analyses indicate an average composition:—

	Centesimally.		
	From Martinique, by Peligot.	From Guadaloupe, by Dupuy.	From Cuba, by Casaseca.
Water,	72·1	72·0	65·9
Sugar,	18·0	17·8	17·7
Ligneous matter,	9·9	9·8	16·4
Salts,	—	0·4	—
	100·0	100·0	100·0

Such also is the average composition of the cane of the third, fourth, and succeeding years' growth from the parent stock, as shown by PELIGOT's researches on this subject.

THE MEGASS OR MILL TRASH, AFTER PASSING THE ROLLERS.

Sugar,	7·9	7·3
Molasses,	3·0	2·7
Ligneous matter and earthy salts,	38·6	39·5
Water,	50·5	50·5
	100·0	100·0

Analyses by F. N. GILL of canes grown in the Aska district, Ganjam, Madras, East Indies—made in the first fortnight of March on ripe cane. Average samples of chips prepared for "diffusion" from the cutting of whole bundles, weighing from 100 to 120 lbs., taken for analysis:—

	A Good Average Bundle.			A Bundle of Picked Cane.			A Bundle of Cane deteriorated by Drought, less 2 feet of Top.
	2 feet Top.	2 feet Middle.	2 feet Root.	2 feet Top.	Next 2 feet.	Last 3 feet.	
Megass proper,	7·63	8·47	8·3	7·58*	8·65†	8·29	8·47
Sugar,	10·63	13·31	13·37	9·49	13·64	13·85	10·41
Glucose,	2·64	1·51	1·54	2·43	·736	·71	5·20
Ash	·307	·259	·233	·545	·363	·349	·352
Juice	92·37	91·58	91·7	92·42	91·35	91·71	91·53
Water,	78·334	75·612	76·122	79·484	75·628	75·945	75·152
Unknown,	·459	·839	·455	·471	·983	·856	·416
	100·000	100·000	100·000	100·000	100·000	100·000	100·000
THE EXPRESSED JUICES ANALYSING.							
Apparent solids, *i.e.*, degree "balling,"	15·2	17·4	17·0	14·0	17·2	17·2	17·9
Sugar,	11·51	14·55	14·58	10·27	14·93	15·11	11·38
Glucose,	2·86	1·65	1·68	2·63	·806	·775	5·68
Ash,	·333	·283	·255	·59	·398	·381	·385
Unknown,	·497	·917	·485	·51	1·076	·934	·455
EQUAL TO, IN THE 100 OF APPARENT SOLIDS.							
Sugar,	75·72	83·62	85·76	73·35	86·8	87 84	63·57
Glucose,	18·81	9·48	9·88	18·78	4·68	4·50	31·73
Ash,	2·19	1·62	1·50	4·21	2·31	2·21	2·15
Unknown,	3·28	5·28	2·86	3·66	6·21	5·45	2·55
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

* Fibre, &c. 7·36; Silica, Lime, and Trace Iron, ·22.

† Fibre, &c., 8·19; Silica, Lime, and Trace Iron, ·24.

These analyses show a large quantity of uncrystallizable sugar in the top, as compared with the rest of the cane, and a large quantity of "unknown" in the middle as compared with the rest of the cane.

The pure or nearly pure juice, when the green matter is removed, contains—

	Per Cent.
Water,	81·00
Sugar,	18·20
Organic matter, precipitated by lead salts,	0·45
Saline matter,	0·35
	100·00

Cane juice has a specific gravity of 1070 to 1090 —10° to 13° Beaumé. It has been obtained as low as 1046, and as high as 1110, at 80° Fahr. It is opaque, frothy, and of a yellowish green. The green part may be filtered out, leaving a pale yellow fluid, which is almost pure syrup. The green scum consists of chlorophyll, cellulose, ligneous fibre, and albumen. Its analysis, given by AVEQUIN, is—

	Per Cent.
Cerosin—a peculiar wax,	50·0
Green matter,	10·0
Albumen and ligneous fibre,	22·7
Phosphate of lime,	3·3
Silica,	14·0
	100·0

A gallon of juice, weighing about ten and three-quarter pounds, contains about twenty-seven grains of this greenish scum.

A few, out of many, analyses made by Dr. STENHOUSE of the ashes of the cane may be given:—

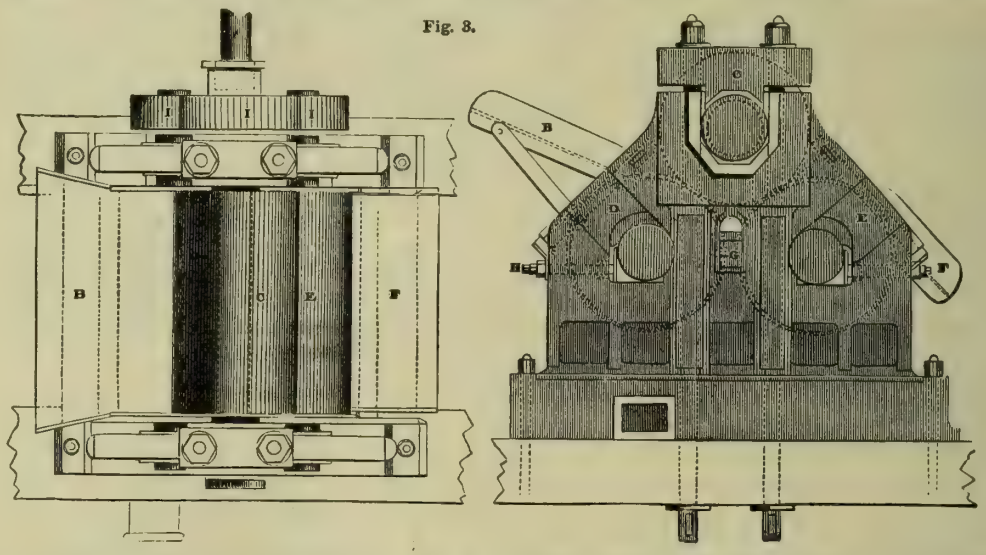
Silica,	46·46	41·37	46·48	50·00
Phosphoric acid,	8·23	4·59	8·16	6·56
Sulphuric acid,	4·65	10·93	7·52	6·40
Lime,	8·91	9·11	5·78	5·09
Magnesia,	4·50	6·92	15·61	13·01
Potash,	10·63	15·99	11·93	13·60
Soda,	—	—	0·57	1·33
Chloride of potassium,	7·41	8·96	—	—
Chloride of sodium,	9·21	2·13	3·95	3·92
	100·00	100·00	100·00	100·00

2. *Extraction of the Juice.*—The sugar exists in the cells of the cane in the state of solution in the fluid, which constitutes the juice or sap of the plant.

The saccharine liquid is extracted from the cane by pressure. The sugar mills employed for this purpose are chiefly three, namely, the horizontal and the vertical roller mill, and the hydraulic press. The latter, however, has not received general adoption. The accompanying woodcut (Fig. 3) shows the construction of the horizontal sugar-mill, which is almost universally used.

The mill—as shown in the annexed Fig. 3—consists of three heavy cast-iron rollers, about 2 feet 4 inches in diameter and 4 feet long, fixed in strong cast-iron frames. The canes are fed from the feeding table, B, and are squeezed twice between the top roller, C, and each of the two lower rollers, D and E. The megass, or solid part of the cane, after being squeezed, passes from the mill by the shoot, F. A trash-turner, G, is placed between the two lower rollers, and under the top one, to guide the canes between the upper and second lower roller. The spaces between the upper and lower rollers are adjusted by the screws, H H; the space between the top and first lower roller should be a quarter of an inch, the second lower roller being set close to the top one. The juice drops into a trough below, from which it runs to the clarifiers, directly if possible; but if the mill cannot be placed sufficiently high to command the clarifiers, a pump is used, worked from the top roller spindle and fixed in a cistern under the trough. The speed found most advantageous for expressing the juice from the canes is at the rate of 20 feet per minute at the periphery of the rollers. The two lower rollers are driven from the upper one by spur pinions, I I I, keyed on the ends of the spindles. The mills are driven by steam, as shown in the drawing, Fig. 4; but sometimes water or wind power is used, according to the physical character of the country in which it is used.

Fig. 3.



A cane carrier is often used to supply the canes to the horizontal mill. It consists of two endless pitch chains working over barrels, the upper one being driven from the spindle of the top roller by spur-wheels or another endless pitch chain. On the outer side of the chains are attached boards sliding over a wood framing, with a ledge on each side to keep the canes on the carrier. The top of the carrier is level with the top of the feeding table, and extends some 30 feet from the mill. The canes are delivered on the carrier instead of on the feeding table of the mill, which facilitates the work, besides causing the mill to be more regularly supplied with canes than when they are delivered on the feeding table of the mill.

A great deal depends upon the right adjustment of the distances of the three rollers, a too near approximation causes, on the one hand, an increased expenditure of force in the working of the mill, and on the other, a too great distance allows a portion of the juice to escape extraction, and to be carried off in the megass. The distance between the feeding roller and the upper one is about half an inch; the delivering roller is still closer to the upper one. In feeding a horizontal mill, the canes are cut into lengths of about 3 feet, and so spread upon the feeding board that these may overlap one another as little as possible. Mills have also been constructed with five and with four rollers. When five rollers are employed three are placed below and two above. A five-roller mill is said to extract 10 per cent. more juice from the cane than a three-roller one; but the megass is thereby much broken, and a much greater expenditure of mechanical power is required to work the mill.

The following are the experiences of Dr. Evans in regard to the advantageous working of a sugar mill:—1. The rollers should be approximated as closely as the work which they have to perform will admit of. In mills in which the rollers observe a vertical direction, the space between the first and second should scarcely, if at all, exceed a quarter

of an inch, whilst a distance of one-sixth of an inch is the most that should be allowed between the second and third. When they are placed horizontally, the upper one should be distant a space of one-fifth to a quarter of an inch from the two lower. 2. The velocity of the rollers should be rendered as uniform as possible, not by diminishing the amount of the motive power, but by a carefully regulated supply of canes. 3, 4. The megass should be invariably repassed between the rollers, so as to extract as much as possible the juice which still remains in it. When canes are rich, and their juice of considerable density, the megass should be sprinkled with a little water, or, where it is practicable, exposed to the action of steam before it is submitted to the pressure; but when the canes are large, green, and watery, this may be dispensed with.

The amount of juice obtained from the cane is not always a criterion of the comparative yield in sugar. The drought or humidity of the season preceding the cutting of the canes determines the presence of a less or greater amount of water in the cane, while the quantity of sugar remains for a time unaffected. Between moist and dry seasons, and thorough and imperfect crushing, the yield of juice may vary from 50 to 75 per cent. of the weight of the canes employed.

3. *The Purification of the Juice.*—The removal of impurities from the juice, as it is delivered from the mill, may be divided into two processes, defecation and clarification.

The crude cane juice contains, besides sugar and water, the impurities—earthy insoluble particles, fragments of the crushed cane or megass, albumen, caseine, wax, soluble colouring matter, and soluble salts. The coarser of the insoluble particles are sometimes removed mechanically previous to the process of defecation. But certain of the nitrogenous impurities of the crude juice, if left in contact with the juice, speedily determine its fermentation, thereby occasioning loss of sugar; and owing to the subsequent conversion of the alcohol, generated by fermentation, into acetic acid, causing the corrosion of the metallic portions of the machinery, and the introduction of metallic acetates into the sugar. It is of the greatest importance that the process of defecation, whereby the nitrogenized compounds are removed, should follow with as little delay as possible upon the extraction of the juice. For this reason the storing of the juice in tanks until a sufficient quantity is obtained for purification is to be reprehended. The first filtration also should, for the same reason, be performed as rapidly as possible. This filtration is effected through a double sieve, the metallic meshes of the first sieve being about one-twelfth, those of the lower about one-thirtieth of an inch asunder. The juice is run from these sieves, or directly from the crushing mill, through a wooden gutter lined with lead to the clarifiers. These are a series of copper cauldrons capable of holding from 3000 to 4000 gallons each. The bottoms of the clarifiers are usually concave, being bulged inwards from below. Each cauldron is provided with a separate fire, the flues from which run into a common chimney, and each fire is provided with a separate damper for regulating or stopping the draught.

Defecation.—Lime is the agent most frequently employed in defecating the juice. The lime should be thoroughly burned and quickly slaked with hot water, enough water being added to give the consistence of a cream. This should be then filtered through a fine wire sieve in order to remove silicious particles and fragments of unslaked lime or unburned limestone. When the juice in the clarifiers has attained the temperature of 130° Fahr. successive portions of the cream of lime are added, until the acids in the juice—acetic and lactic, &c.—have been completely and exactly neutralized, which is shown by the neutrality of the liquor to blue and red litmus paper. The mixture of juice and lime is thoroughly incorporated with an oar, and the whole left to digest for about a minute. The portions of cream of lime successively added to effect neutrality should not contain more than about 4 ozs. of solid lime per gallon. After neutralization by cream of lime, as above described, the heat is urged until a temperature just below the boiling point of the liquor is reached. A thick scum is then formed upon the surface of the liquor, and the clarification is judged complete when this scum breaks and a white froth appears in its interstices. In all cases an excess of lime is to be avoided, partly because nitrogenous matter, upon the removal of which, from an acid solution by heat and lime, the clarification in a great measure depends, is redissolved by an excess of this agent, but mainly because of the destructive action of caustic alkalies on the glucose present. If, however, an excess of lime has been added, it may be remedied by the addition of small quantities of a solution of alum. When this salt is added to any alkaline solution with excess of lime, its alumina is precipitated and rises with the same, fixing a portion of the colouring matter of the juice at the same time, and thus assisting in the clarification. Of the simultaneous products found in this reaction, *videlicet*, sulphate of lime and sulphate of potassa, the first is in a great measure insoluble and rises with the scum; the second, however, is soluble in the liquor, and cannot be subsequently separated from it; and this is the only drawback in the employment of alum to neutralize overlimed juice. Sulphate of alumina, however, is not subject to this disadvantage, and may, therefore, advantageously replace alum in the neutralization of overlimed juice.

Other substances have been employed for the defecation of cane juice, of which the principal are nut-galls, sulphate of zinc, alum, sulphate of alumina, sulphuric acid and lime, and subacetate of lead, but as they have not found their way into use, a more particular description of their application is unnecessary.

Though the defecation by lime alone is still that most frequently employed, several substantial improvements have been effected during the last few years—*e.g.* the process of Jcery—who adds to the juice an excess (*i.e.* more than will dissolve) of the

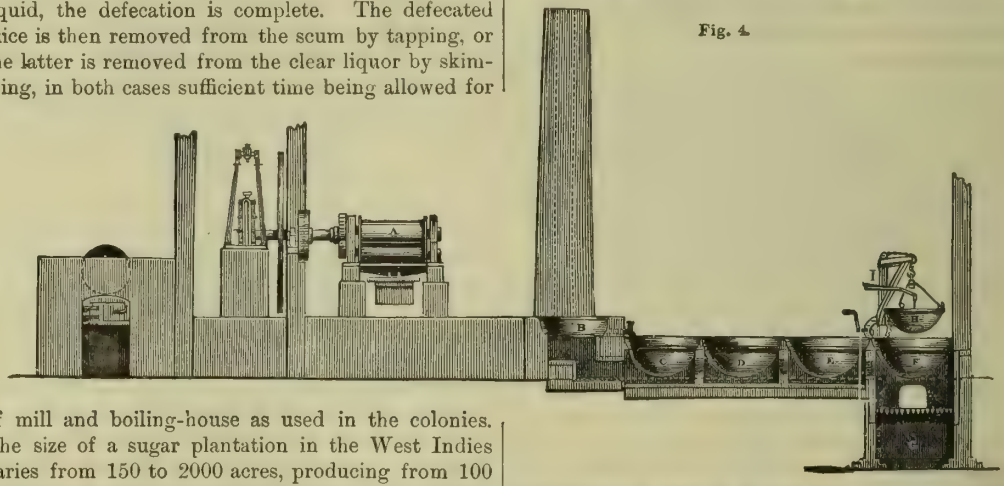
very slightly soluble mono-sulphite of lime, and heats the liquor to boiling as usual. The natural acids of the juice dissolve and decompose an equivalent amount of this salt, being themselves neutralized by its base lime, and setting free their equivalent of sulphurous acid, which in its turn causes a more complete coagulation of the albuminous constituents of the juice than heat alone, and also exerts an appreciable bleaching effect. The mono-sulphite of lime is prepared by passing the fumes of burning sulphur into milk of lime till all alkaline reaction is lost—the pale yellow and somewhat sandy product of this operation is the body in question. A modification of Jcery's process, now much employed, consists of treating the juice with sulphurous acid gas, either in the defecating pan, or on its way there from the mill, and subsequently neutralizing the excessive acidity so produced by the cautious addition of lime.

When the scum has risen to the surface, and the clear liquor is seen through its cracks, the approach of which point is usually judged of empirically by the equalization in size of the bubbles formed in the liquid, the defecation is complete. The defecated juice is then removed from the scum by tapping, or the latter is removed from the clear liquor by skimming, in both cases sufficient time being allowed for the heavier portions of the scum to subside. As the scum always contains a considerable portion of liquor in its pores, it is generally submitted to pressure in a simple lever press, and the extract added to the liquid which has been tapped off.

In those countries where fuel is cheap, and especially in those manufactories where steam is employed, either as a motive power for the mill, or for the vacuum pan —afterwards to be described—or for other purposes, the heating of the defecating pans is sometimes effected by means of steam. It is clear that as the temperature requisite for boiling in the open air is above that of boiling water, the steam by which it is effected must be either superheated or high-pressure steam. And as in most sugar growing lands fuel is scarce, and as a great use of fuel attends the application of superheated steam, high pressure steam is employed. This is usually conveyed by a copper worm through the pan, the steam passes downwards round the spirals of the worm, and the condensed water is discharged under pressure.

Sugar Mill.—Fig. 4 represents the arrangement of mill and boiling-house as used in the colonies. The size of a sugar plantation in the West Indies varies from 150 to 2000 acres, producing from 100 to 5000 hogsheads of sugar per annum. The boiling-house should be situated in a central position on the plantation, to avoid loss of time in carriage of the canes from the fields to the mill (the mill, A, has been already described in detail).

Fig. 4.

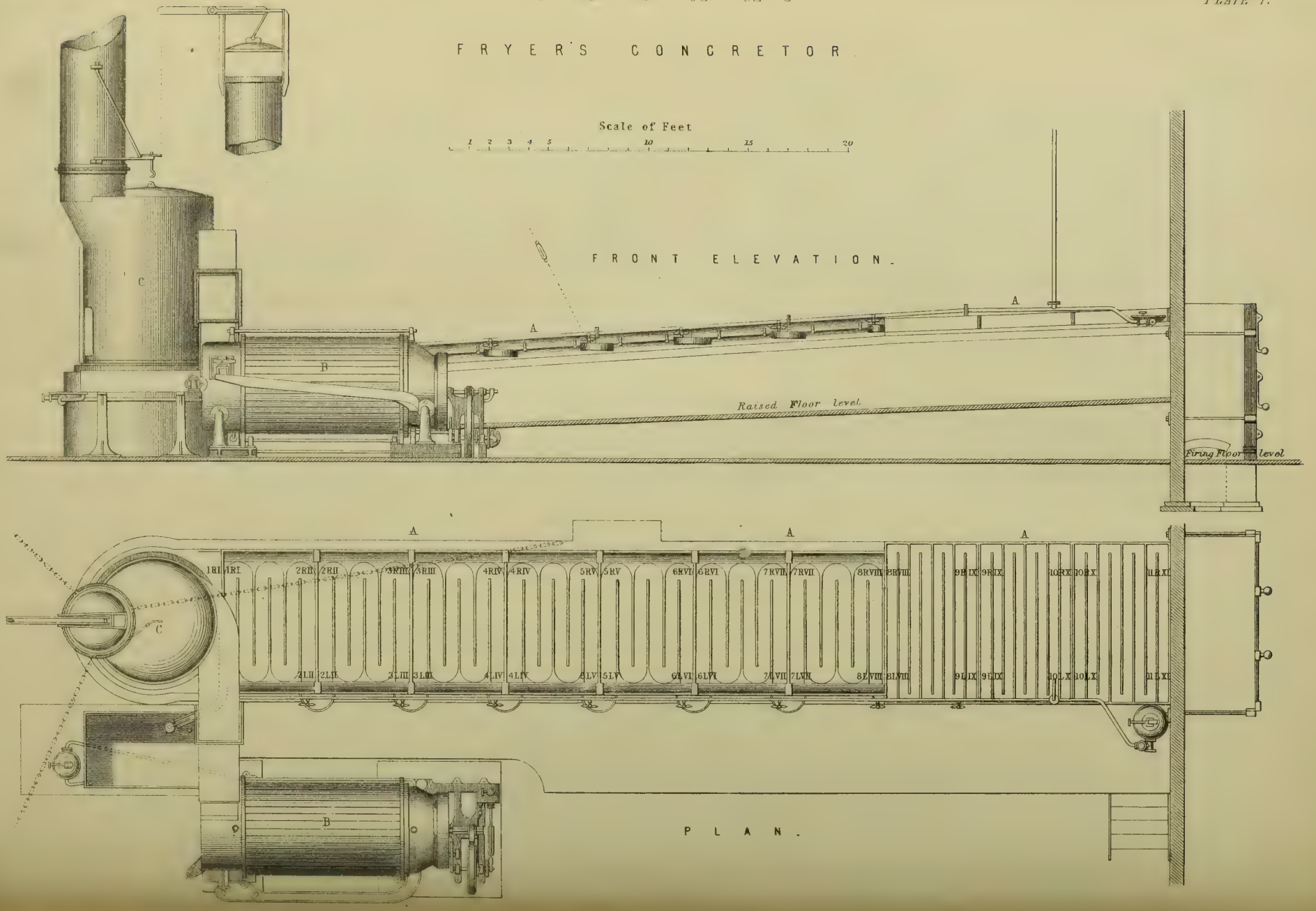


Clarifiers.—The juice, as it is expressed from the canes, runs into the clarifiers, one of which is shown at B, Fig. 4. Two are generally used, one filling while the juice in the other is clarifying. They are generally cylindrical copper pans, with crown or arched bottoms, to resist the action of the fire. They are fitted with a large cock at the bottom for running the juice into the first copper. They are set in brickwork at the end of the battery, the flame passing under them previous to going into the chimney, a damper being provided to each to direct the flame under the one that is full. Milk of lime is added sufficient to neutralize the acid in the juice.

The battery is a range of pans, C D E F, with the furnace, G, at one end. The fire passes under the range, and under either of the clarifiers to the chimney. The pans are hemispherical in shape, diminishing in size from the first copper, C, under the clarifiers, to the "striking teach," F, in which the evaporation is completed. As the juice becomes concentrated in the pans nearer the furnace, they are filled up from those behind them, until the striking teach is sufficiently full, and the sugar in it concentrated to the granulating point. It is then ladled into shallow wooden vessels, where it is allowed to cool, and from thence it is conveyed into the hogsheads in the curing-house. An improved method of ladling from the striking teach to the coolers is now much used. A copper pan, H, fitting the inside of the striking teach as accurately as possible, has a large valve opening towards the inside worked by a lever, I, over the side, and a chain from the ground. The dipper is attached to a crane, J, which commands the striking teach and a gutter to the coolers. The advantage of the dipper is that the striking teach can be emptied and refilled in much less time than by the ladle, and consequently there is not so much risk of burning the copper and the sugar. A gutter is

SUGAR.

FRYER'S CONCRETOR



J. B. LIPPINCOTT & CO. PHILADELPHIA

made in the brickwork at the side of the battery, into which the impurities that rise to the surface of the liquor are skimmed. The skimmings, from which are distilled the best rum, are conveyed from the gutter to a tank previous to fermentation. The floor of the curing house, in which the molasses is drained from the sugar, is composed of a series of gutters which incline to the centre of the building, and deliver their contents to a main gutter which communicates with a tank for the molasses. The hogsheads are placed on end over the gutters, small holes being bored in their ends for the passage of the molasses. The sugar, after remaining in the curing-house about fourteen days, is ready for shipment, and is known in the market as raw or muscovado sugar.

The megass, after passing through the rollers of the mill, is dried and used as fuel for the battery; being better suited for that purpose than any other convenient fuel, as far as heat goes, a very quick fire being required. A saving of fuel is effected by placing the boiler of the cane-mill engine at the end of the battery, so that the products of combustion may pass from the battery through the boiler flues, previous to going into the chimney. A furnace is fitted to the boiler for use before the battery is at work in the morning, and which can be shut off when not required, the waste heat from the battery being almost sufficient to work the boiler for the cane-mill engine.

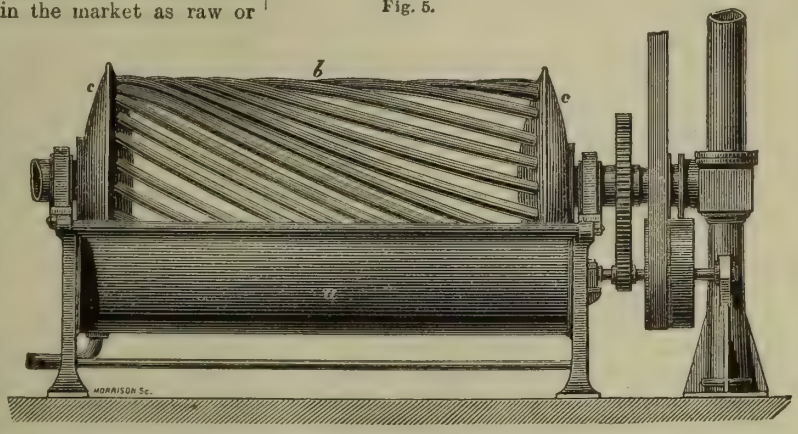
In the striking teach of the ordinary battery there is a liability of the upper part of the teach becoming overheated, and so making the sugar of a darker colour when it splashes up against it, depreciating its value. A pan made so that the heating surface is entirely covered with liquor is used in some places, called a *bascule* or "tilt-pan." It is a shallow, cylindrical, copper pan, about five feet diameter and two feet deep. It is furnished with a lip to run off the sugar, and works on a hinge under the lip. The pan is set over a fire, and when the sugar is boiled to the granulating point, it is tilted up by a lever and chain fixed to it. The sugar being turned out at once into the cooler, there is not the same risk of burning as in the ordinary fixed pans.

Rectangular copper pans with crowned bottoms have also been substituted for the hemispherical pans with cocks or valves, to empty them from the bottom. They are ranged side by side over the furnace, so that the flame runs under them from end to end; and there being no side flues, the metal of the pans does not become heated, and consequently the quality of the sugar is not injured.

The rough and ready method of boiling down the juice over the open fire just described, results, as might be expected, in great destruction of sugar, and production of those brown products of its decomposition, which go by the collective name of "Caramel." Accordingly, many attempts have been made to substitute an apparatus which should concentrate the clarified juice at a lower temperature than is possible in the train of open fire-heated pans. Three only of the many forms devised have held their own. The triple-effect vacuum pan (See Beet-root Sugar), Wetzel's pan, and Fryer's concretor.

Wetzel's Pan.—The construction of this useful piece of machinery is evident from the cut annexed. The juice is admitted into the steam jacketted trough, *a*, into which dips about half the circumference of a cylinder of curved copper pipes, *b*, which communicate at each end with the hollow copper dishes, *c c*, which are, with the connected pipe, *b*, supplied with low pressure steam through *d*. When at work, *a*, *b*, *c*, is caused to rotate by the gearing shown. The hot liquor is thus kept moving, and thin films of it spread over the surface of the pipes are exposed to the atmosphere, so that evaporation takes place very rapidly, and consequently the temperature does not rise much above 150° to 170° Fahr.

Fig. 5.



Fryer's Concretor.—In this apparatus (see Plate I.) the clarified juice is evaporated very rapidly, by being made to flow in a thin film over a large inclined surface, mantained at a high temperature by direct fire heat. The extreme rapidity with which each portion of juice is concentrated to the desired point, or in other words, the very short time during which the juice is exposed to the action of the high temperature, prevents any serious amount of injury to the quality or colour of the product. The details of the construction and manipulation of this simple and effective appliance of the sugar maker are best given in the words of the inventor, Alfred Fryer:—

"This machine has been called into existence by the belief that it is not the interest of the planter to compete with the refiner, but to produce the largest possible quantity of a material suitable for him to operate upon. The end aimed at by the concretor is then to concentrate as cheaply and efficiently as possible the juice which is supplied to it; turning it at once into a solid substance, which is easily

packed, and is not subject to loss by drainage. To accomplish this end, the clarified juice is first run over a series of shallow trays, A A, in a stream of about half an inch deep, these trays are divided by ribs running from one side nearly to the other, so that each tray forms a continuous narrow serpentine channel, in traversing which, the juice passes six times from side to side of the tray.

"In the largest size, there are ten of these trays placed end to end, and having connections so arranged that the juice can flow freely from end to end of this series, thus (the length of the series of trays being about 48 feet) the juice has to traverse nearly six times this distance before it passes away to undergo a further process of concentration in the revolving cylinder.

"Heat is applied to the bottom of these trays by means of the furnace the flame of which passes under the whole length; the juice is concentrated by means of this process to a density of from 30° to 34° Beaumé. After leaving the trays the juice passes into the revolving cylinder, B, where it is made to expose a very large surface to the action of heated air drawn through the cylinder by means of a fan. The air itself is heated by passing amongst and around a number of tubes in the air heater, C, through the inside of which tubes the products of combustion pass to the chimney.

"In this cylinder the concentration is continued until the material has attained such a consistency that it drops in large flakes instead of flowing in a continuous stream. When this degree of consistency is attained, it is discharged from the cylinder into casks, or any other convenient receptacle, and in cooling becomes a solid mass, which without any further manipulation is ready for shipment.

"The whole of the operations mentioned above do not occupy more than about half an hour, while the supply of the juice to the machine and the discharge of concrete from it are each of them continuous, or nearly so, both objects being effected without stoppage and without any interference with the working of the machine.

"No molasses is made, but the average yield of concrete is about 2 lbs. to the gallon of juice, gauging 10½° Beaumé. The material thus produced sets into a solid mass, which contains uninjured in quality or colour all the saccharine matter held in the juice from which it is made; it is not subject to any perceptible drainage on the voyage to England, and is precisely the article required by the European refiners."

If the juice has (after defecation) been simply concentrated to 30°—33° B. by the use of the Wetzel pan, triple effect, or Fryer's concretor used without the terminal cylinder, it must be brought to a granulating point by further evaporation, which is sometimes effected in an open fire-heated pan, as previously described in connection with the "Jamaica train," but which should always be carried out in the "vacuum-pan."

Curing the Sugar.—Supposing the sugar granulated, the manufacturer has a pasty mass of small sugar crystals imbedded in a coloured adhesive syrup, and his next task is to separate the latter from the former so far, that the "sugar" shall not retain enough syrup to subsequently drain to an appreciable extent during travel or storage.

The old and still largely used method is to fill the granulated and cooled mass into open hogsheads, standing on racks over a large cistern, and allowing the syrup to slowly drain away by gravitation through holes in the bottom, which are loosely stopped by plantain stalks. The other method, which is generally employed for the better class of vacuum pan sugars, is by the use of the centrifugal machine. In the latter case it is generally advisable to render the cool, set mass of granulated sugar somewhat more fluid by mashing it up with some extra syrup, in order to facilitate its even distribution in the sieve of the centrifugal, so as to promote even drainage, and diminish the severe vibration which occurs when the centre of gravity of the rotating mass does not coincide with the centre of revolution.

The syrups separated from the first crop of raw sugar are, when good enough, reboiled to granulating point, and a second crop of sugar obtained. As this syrup is more impure than the original juice, crystallization is slower and less perfect, the grains are consequently smaller, and finally retain a larger proportion of darker and still more impure syrup, and the "sugar" is therefore of much lower quality. The raw cane sugar, prepared in one or other of the ways described, or by the still rougher methods in use in India and China, varies of course in composition with the quality of the juice brought into working, and with the process employed in its manipulation.

The juice of the cane contains, as a rule, but a very small proportion of solid bodies other than sugar, as will be seen on reference to the analyses previously quoted; and among these bodies other than sugar we may include the invert sugar, or as it is sometimes called, the fruit sugar. This is present in the juice of ripe healthy canes in relatively small proportion, yet, nevertheless, the raw sugar and molasses prepared from such canes contain large quantities, produced by the destruction of the valuable cane sugar.* This destruction is brought about by several causes—first, and most important, is incipient fermentation, which comes on with great rapidity under the influence of heat and moisture, firstly in the cane itself, at all cut or bruised surfaces, and secondly in the expressed juice, which of course contains a leaven of already formed ferment from the before-mentioned source. As fermentation, once begun, spreads through the liquid with great rapidity, it is evident that it is of the utmost importance to put an end to the conditions under which it can take place with the least possible delay. Thirdly, a slow fermentation occurs frequently in the potted and even in the cured sugar, resulting in

* The glucose found in "raw sugars" is not "invert sugar" simply, for as a matter of fact it is optically inactive, or nearly so, in the large majority of cases. "Concretes" not unfrequently contain lævo-rotatory glucose.

the production of molasses, which drain away and cause the annoying loss of weight during the voyage to market. The first action of ferments on cane sugar is to "invert" it—*i.e.*, to change it into a mixture of dextrose and lævulose—and the subsequent one, to change one or other, or both, of these sugars into some quite distinct body, such as alcohol, acetic acid, butyric acid, or gum, according to the nature of the peculiar ferment in action. Acetic acid is one of the substances most commonly produced during the fermentation of cane juice; and as it in its turn causes the "inversion" of a further quantity of sugar when the liquid containing it is heated, its formation is doubly harmful. The only available means of preventing or arresting the fermentation of cane juice is to heat it at once to a temperature of at least 160° Fahr. Sulphurous acid and the sulphites somewhat check and delay the inversion of the sugar at ordinary temperatures, and go very far in preventing the subsequent formation of acetic acid.

The prolonged action of water at a high temperature is said to cause a great amount of inversion; but it is doubtful whether *pure* water has any considerable action at any temperature which occurs in the process of sugar making. But as the inverting power of all weak acids increases very rapidly with the temperature, and is proportional to the time during which they act, it is obvious that it is of great importance to evaporate all saccharine solutions at as low a temperature and with as great a speed as possible.

Diffusion applied to Cane.—Here and there of late years the so-called "diffusion process" has been applied to the extraction of sugar from the cane. It was first adopted at the Aska Works, Gangam, Madras, and has there been found to yield results far superior to the mill—the total sugar, with molasses, being 30 to 45 per cent. greater, owing to the far more perfect extraction of the juice in the first case. Not only is the sugar removed more perfectly from the trash, but the juice is so much purer than ordinary mill juice, that after neutralization with lime it has a pale sherry colour, and gives an insignificant amount of scum on boiling. The sole difficulty of the process lies in keeping the knives which slice the cane sufficiently sharp.

The following table exhibits the actual results of some comparative experiments carried out in Louisiana on the comparative yield by the "mill" and "diffuser":—

Process.	Days Running	Lbs. Cane Worked.	Lbs. Products.		Per Cent. Sugar	Per Cent. Syrup.	Total Per Cent.	Surplus Per Cent.			Cost of 100 lbs. Sugar and Molasses.	Per Cent. Dry Substances Obtained.
			Sugar.	Syrup.				Sugar.	Syrup.	Total.		
Mill, ...	6	1,386,730	57.743	43·17	4·164	3·113	7·277	—	—	—	$46·88	6·51
Diff. (1st),	6	987,945	51.706	50·778	5·234	5·139	10·373	25·7	65·1	42·54	39·2	9·14
Diff. (2nd),	5	915,515	54.549	38·752	5·958	4·233	10·191	43·0	35·98	40·0	38·35	9·15

The advantages and disadvantages of the diffusion process over the mill may be summed up—the cane gives 40 per cent. more sugar and syrup, but about ten extra hands are required in the mill itself, and the juice obtained requires 25 to 30 per cent. more fuel to boil it down.

The following analysis of megass from the diffusers at Gangam should be compared with that by Peligot of ordinary mill trash already given:—

	Just out of Diffuser.		After Drying, ready to be used as Fuel.	
Mineral matter of Megass,	·33	Megass proper.	2·33	
Fibre and cellulose,	11·17	11·5	77·14	Combustible matter.
Sugar,	·413	—	2·85	82·214
Glucose,	·076	—	·526	
Gums, albumens, &c.,	·245	—	1·698	
Ash,	·066	—	·456	—
Water,	87·700	—	15·000	—

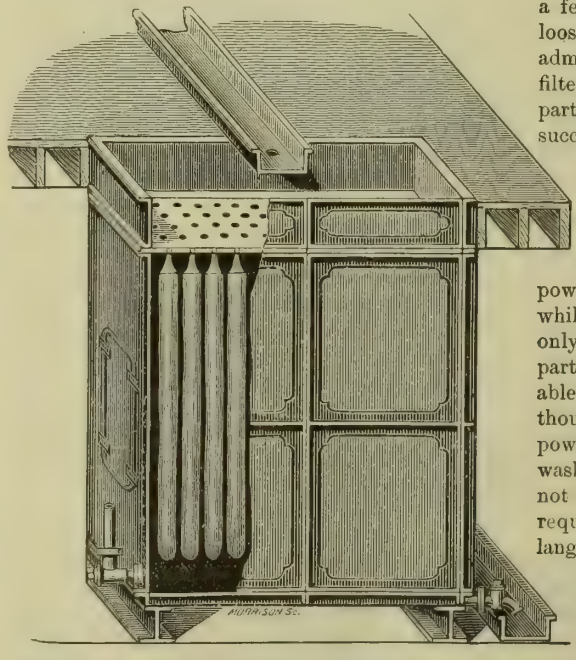
Sugar Refining.—The refining of raw sugar may be treated very shortly, since it resolves itself simply into removing solid impurities by mechanical filtration of its solution; colouring matter, and other soluble organic matter, more or less completely, by animal charcoal; and then causing it to separate as crystals from the clean solution by evaporation at a low temperature, and removing the mother liquor from those crystals, more or less completely, by suitable means.

Blowing Up.—The "raw sugar," whether cane or beet, is turned out of the bags, hogsheads, &c., in which it arrives at the refinery into cast-iron tanks, holding from 3 to 6 tons of sugar at a charge. These "blow-ups" are as a rule, and should always be, provided with mechanical stirring gear. Water is added, and steam turned on to the close copper worm or open perforated pipe, with which each "blow-up" is provided, and the agitator kept at work till the sugar is all "melted" (dissolved). The workman brings the "liquor" to a fixed density by gauging with a Beaumé float, and adding more sugar or more water as required. The question whether "close" or "open" steam is the better, is not of much importance; for if the open steam makes the sugar and its solution locally hotter than the close worm, it does its work in half the time, so the gain balances the loss. The "thickness" which the liquor should have depends on the purpose which it is to serve, and varies from 25° B. to 33° B. Blood or other form of liquid albumen is still largely used in the blow-ups by those who melt very low raw sugar. It is added to the sugar solution before this attains a temperature of 160° Fahr., and well mixed in; the temperature is then raised nearly to boiling point, when the albumen coagulates and forms a network of glutinous fibres, which embrace and entangle small floating impurities, and carry them to the surface in the form of a scum, from which the liquor below can be strained off by a sieve or perforated plate, thereby relieving the bag filters of part of the work they would otherwise have to do. Powdered animal charcoal is

sometimes used in addition to blood, but the advantages of so doing are doubtful. Small quantities of lime, chalk, magnesia, sulphate of alumina, phosphoric acid, &c., are sometimes added to improve the clarification; but with the exception of lime and chalk, none of them seem to retain their footing in the refinery. The temperature at which the raw sugar is melted (finally) varies in different houses from 140° Fahr. to 215° Fahr.—the makers of the half-refined pieces mostly employing the lowest temperatures.

Bag Filters.—From the blow-ups the liquor runs on to the bag filters, which consist of a number of twilled cotton bags, about 2 feet wide and 5 or 6 feet long, drawn into an outer sheath of hemp meshing, to prevent their expansion when filled with liquor. Each bag, to the number of 50 to 200, with its sheath, is tied on to a bell-shaped copper nozzle, which screws into holes on the lower side of the bottom of an iron tank, which receives the liquor from the blow-up. The bags are surrounded by an iron casing to keep them hot, and to collect the clear liquid as it drains through. The outlet of each filter-case is provided with means of diverting any portion of liquid which runs foul to a separate tank. Fig. 6 shows a bag filter made by Messrs. D. Stewart, Glasgow.

Fig. 6



The washing of the bags and the solid impurities ("scum") which they have retained is one of the most troublesome and unsatisfactory operations of the refinery. One method generally employed to remove the sugar in the scum is the obvious one of running hot clean water on to the filters after the sugar, so as to wash the latter through. This is effective, but rots the bags, and makes a large quantity of thin water, which must either be evaporated by itself or used for dissolving fresh raw sugar. The other method is to turn the scum out of the bags, wash the latter by themselves, boil up the scum with a small quantity of water, and then press it in cloths. This is equally effective, and makes much less thin liquor.

The bag-filtered liquor next passes to the char-filters to be more or less decolorized. In English refineries these filters are generally very large—from 5 to 9 feet in diameter and from 15 to 30 feet deep, and holding from 7 to 50 tons of animal charcoal each. The animal charcoal ("char") with which these filters are filled must have been recently heated to redness, and then allowed to get quite cool before use. How or why char used too recently burnt and warm gives bad-coloured liquor is not settled, but the fact seems to be admitted.

The hot liquor is run on to the top of the char in an *uninterrupted* stream, till it begins to run from the cock on the pipe at the lowermost end. This latter is then closed for two or three hours to allow the char to settle into its place, and the fine particles to attach themselves to the coarser, so as not to flow off with the liquor and render it turbid. It should have been stated that in filling the char cisterns, the false perforated bottom is first covered with a moistened blanket, which is folded in carefully round the edge of the cistern, and then covered by a few inches of char by hand before emptying the loose char in from the top. As the raw liquor is admitted at the top of the column of char and the filtered liquor flows away from the bottom, the first particles which get through come in contact with successive fresh portions of char which have not yet done work, while all succeeding portions meet char which has its power more or less exhausted; consequently the first portions of liquor coming through are the most perfectly decolorized. The uppermost portion of the char column has its power of decolorizing and absorbing rapidly used up, while the lowermost layers, from coming in contact only with liquid which has already parted with a great part of those constituents which are readily absorbable by animal char, is comparatively fresh. Still though more than half the char may have its original power but little impaired, the cistern has to be washed off and the whole reburnt, because there is not enough perfectly fresh charcoal to give the required amount of decolorization (in sugar-house language, "to give enough colour"). By connecting the bottom of a cistern which has reached this stage with the top of a fresh one, and forcing the liquor through by hydraulic pressure, the char in the latter receives liquor which has been partly deprived of its impurities in the lower part of the first, and consequently has but little work to do. This working in battery, as it is called, is but little practised in England, though very common among the beet sugar-makers of the Continent.

The washing off of the char cisterns is effected by admitting hot water at the top, either before or after expelling most of the thick liquor by com-

pressed air, and allowing it to percolate slowly downwards, carrying before it the thicker and heavier sugar liquor. As might be expected, there is much dilute sugar solution ("sweet water") made in washing out such a porous material as animal charcoal thoroughly soaked in strong sugar solution; and this "sweet water" constitutes a difficulty for the refiner, for the water does not dissolve out the sugar alone, but unfortunately extracts from the char a large portion of those impurities, both mineral and organic, which had previously been absorbed from the strong sugar solution, as if the char had been able to remove them from a solution in which they were only just soluble, but could not retain them in presence of a more powerful solvent, like water. This sweet water is usually treated in the same way as the scum water of that particular factory.

The mode of action of animal charcoal in effecting the decolorization and purification of, say, sugar solutions, is a matter of constant discussion, if not of dispute. As animal charcoal, like other porous forms of carbon, absorbs and condenses in its pores many times its own volume of the atmospheric gases, and retains oxygen with special obstinacy, it has been imagined that the decoloration produced by it was really a bleaching by oxidation. But this assumption is entirely disposed of by the following experiments:—A portion of animal charcoal inclosed in a test-tube, which was drawn out and connected with a Sprengel mercury pump at the open end, was kept ignited to redness, while the pump was at work, till all gases so removable were extracted (and at any rate all oxygen combined with carbon). The drawn off portion of the tube was sealed while the vacuum was maintained. This little tubeful of exhausted char was dropped into a long, wide tube closed at one end, and containing a solution of caramel, indigo, or carmine, as the case might be. This wide tube was drawn off to a neck, the air exhausted by the mercury pump, the liquid boiled for a considerable time, and the whole sealed up. The tube containing the char was then broken by shaking, and it was invariably found that the decolorization produced was as great as that by an equal weight of untreated char on an equal volume of the coloured solution in the air.

Again, Scheibler has shown that char ignited in hydrogen decolorizes solutions in an atmosphere of hydrogen.

The absorption of lime from sugar solutions has similarly been shown to be independent of absorbed carbonic acid. But when animal char which has been used to decolorize a solution of carmine is digested with alcohol, the carmine is again dissolved out without sensible loss; and so with other coloured and colourless bodies, a sufficiently powerful solvent withdraws them from the charcoal. It seems, therefore, that "char" acts like linen, cotton, or silk fibre in a dye stuff, and abstracts a portion of the colour, gets dyed, in fact; and as, say, cotton will not take up all dyes equally, so char will absorb certain colouring matters either very little or not at all, and others largely and freely. The liquor as it leaves the char is received in tanks, from whence it goes to—

The Vacuum Pan.—The vacuum pan is universally employed for evaporating the water from solutions of sugar in refineries and in beet-root sugar factories, and is largely used by the more intelligent and enterprising of the manufacturers of cane sugar. The object of this important piece of apparatus is to effect the evaporation of the water rapidly, and at a lower temperature than is possible by heating in open vessels. At ordinary atmospheric pressures, solutions of sugar of the following strengths boil at the temperatures given (Gerlach):—

Per Cent. Sugar.	Boiling Point. Degrees Fahr.
0,	212
10,	212·7
20,	213·4
30,	213·8
40,	214·7
50,	215·6
60,	217·4
70,	223·7
79,	233·6
91,	266·0

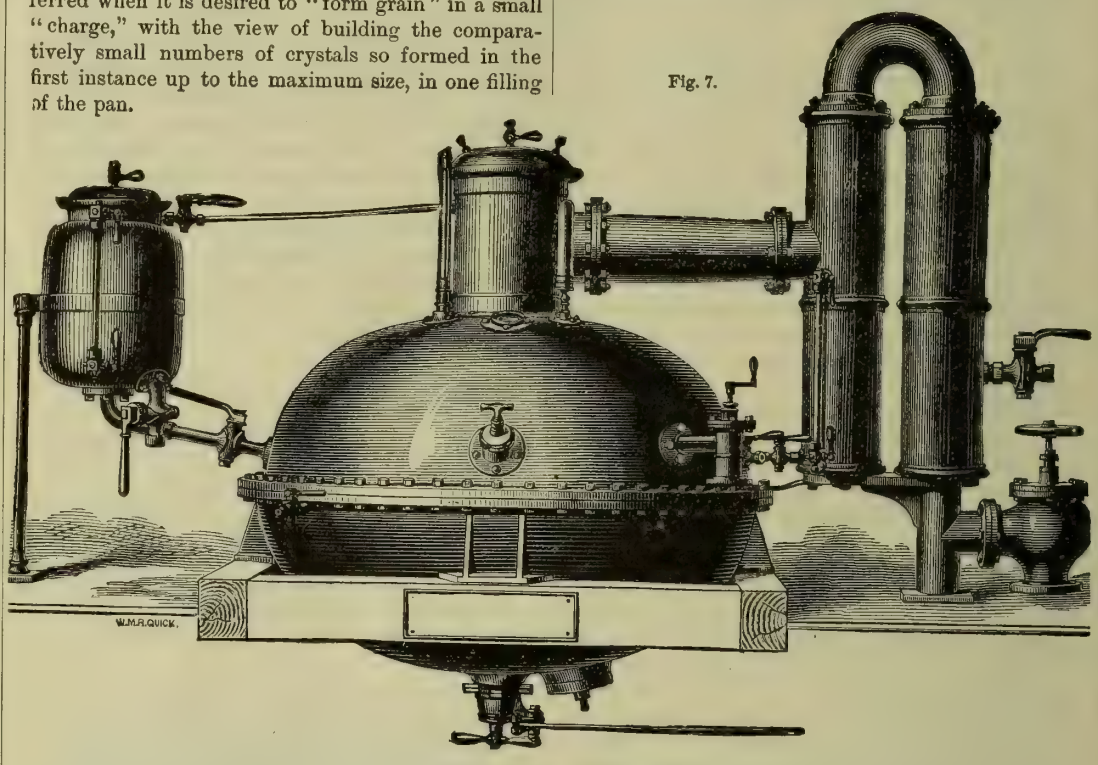
While the most concentrated of these solutions will boil vigorously at 120° Fahr. in a good vacuum pan, and will consequently suffer less from the action of a high temperature than if heated over an open fire.

Boiling is the giving off of bubbles of vapour by a liquid, and this will occur at any temperature, when the tension or elastic force of the vapour of that liquid exceeds, by ever so small an amount, the pressure on the liquid. In a first-class air-pump vacuum, water will boil freely at freezing point (32° Fahr.), while under great pressure it may be raised to 300° or 400° Fahr. without boiling.

The general construction of the vacuum pan itself needs little description beyond reference to the accompanying cut (Fig. 7). The shape of the pan is of comparatively small importance, except for specific purposes; thus, a broad shallow pan is preferable for those cases where the lowest possible temperature is required, since a column of liquid above the heating surface increases the pressure, and consequently the boiling point of the mass in immediate contact with the worms, to an amount directly proportionate to its height. Thus, if the liquid in the "pan" has a specific gravity of 1·4, and a height of 5 feet above any given point of worm or heated bottom, then these 60 inches will exert a pressure equal to $60 \times \frac{1{\cdot}4}{13{\cdot}6} = 6{\cdot}2$ inches of mercury nearly on the particles of liquid in contact with that point; and consequently before they will boil, they must be heated to a temperature as much above that of the uppermost stratum of liquid in the pan as is equivalent, in sugar-house language, to a vacuum 6·2 inches worse. Though this excessive heating is only momentary, because of the general violent motion of the boiling mass carrying the hot portions into a position where they attain a temperature corresponding to a less pressure; still with low products, which are delicate,

some "loss of colour" is produced. Pans with rather pointed constricted bottoms are to be preferred when it is desired to "form grain" in a small "charge," with the view of building the comparatively small numbers of crystals so formed in the first instance up to the maximum size, in one filling of the pan.

Fig. 7.



Steam and Water required to Work a Vacuum Pan.—Let it be supposed that 30,000 lbs. (about 13·5 tons) of green sugar (*masse-cuite*), containing 10 per cent. of water, be boiled out of liquor of 50 per cent. sugar contents (27½° B.) in two hours: then 30,000 — 3000 = 27,000 lbs. sugar is in that *masse-cuite;* but that sugar was dissolved originally in its own weight of water, or 27,000 lbs., of which 3000 lbs. remain unevaporated, or 24,000 lbs. of water have been converted into steam in the two hours. Assume that two-thirds of this quantity is evaporated in the first hour, while the contents of the pan are comparatively "thin," then 16,000 lbs. of water vapour have to pass through the neck of the pan and be condensed in one hour. If the pressure in the pan be equal to 2 inches of mercury ("a 28-inch vacuum"), the volume of this vapour will be $\frac{30}{2} =$ 15 times as great as at the atmospheric pressure. According to Regnault's experiments, saturated water vapour of this tension weighs 0·003 lbs. per cubic foot; and leaving out of sight minute corrections, we may take it that under the conditions given, the 16,000 lbs. of water will form $\frac{16{,}000 \times 1}{\cdot 003}$ = 5,333,334 cubic feet of vapour to pass through the neck in 60 × 60 seconds, or 1481·5 cubic feet per second; and if the neck have an area of 2 square feet, the velocity of the vapour must be $\frac{1481{\cdot}5}{2} =$ 740·75 feet per second. With a wider neck, the velocity will be proportionately less, and *vice versâ*, and the resistance caused by friction will vary at the same time; but in what proportion or degree there is, as far as I know, nothing determined. In practice wide and short necks are found to facilitate the maintenance of a good vacuum.

Condensing Water Required.—In the case supposed 24,000 lbs. of water were evaporated in two hours, and were converted into vapour of one-fifteenth of the atmospheric pressure. Now, as the minimum pressure obtainable in any apparatus containing water is that due to tension of the vapour in the coolest part of that apparatus, the air-pump must not have a temperature exceeding 101° Fahr. in theory, and in practice to get such a vacuum not more than 80° Fahr. The colder the pump is kept, supposing the whole apparatus to be tight, the better will be the vacuum, and consequently the colder will the pan boil.

Let us assume, for the sake of simplicity, that all condensing water of the initial temperature of 60° Fahr. runs away at an average of 90° Fahr., and that the vapour from the pan is saturated steam (it is actually superheated), 1 lb. vapour of a tension equal to 2 inches of mercury contains 1145·1 units of heat. The pound of water resulting from its condensation at 90° Fahr. contains 90 of those units, leaving 1055 units to be taken up by the condensing water. Each pound of water heated from 60° to 90° Fahr. absorbs 30 units of heat; so $\frac{1055}{30} = 35{\cdot}2$ lbs. of water at 60° Fahr. are required to condense

1 lb. of steam of the tension given, or 24.000 × 35·2 = 844,800 lbs. = 84,480 gallons required for this one pan of sugar.

For all technical calculations it will suffice to assume that each pound of vapour from the pan contains 1150 units of heat; and then knowing the temperature of the condensing water before and after use, to determine the quantity of it required by the method illustrated above. It must not be forgotten in estimating for the size of pumps, pipes, &c., to supply the water, that the consumption will be much larger in the first part of the boiling than in the last.

Steam Required.—Assuming that there is no loss of heat by radiation, leakage, &c., and that the vapour from the pan is saturated steam of a temperature corresponding to its tension (this last assumption introduces but a slight error), the heat to be communicated by the "boiler steam" in the worms and jacket will be, first, that required to raise the original 54,000 lbs. of liquor (assuming, which is not quite correct, that it has the same specific heat as water) from, say, 100° Fahr. to 130° Fahr., or about 1,620,000 units; and then to convert 24,000 lbs. of water of this temperature into steam, containing 1145 units of heat * per lb. (see *supra*): (24,000 × 1145) — (24,000 × 130) = 24,360,000 units of heat, or 25,980,000 units of heat must be given to the sugar liquor by the steam in the worms and jacket. If the steam used has a tension of 30 lbs. above atmospheric pressure, and the water condensed from it runs away through the condense box at a temperature corresponding to this pressure, or 274° Fahr., then as steam of this pressure contains 1197 units per lb., and the water resulting from its condensation at this pressure contains 276 units, each pound of steam affords 921 units of heat effective for evaporating the water in the pan $= \frac{25{,}980{,}000}{921} = 28{,}208{\cdot}5$ of steam are required, without allowing anything for waste in any way—as by condensing in the pipes, radiation from the pans, &c. If we compare with this the quantity of heat required to evaporate the same quantity of water at atmospheric pressure, as in an open pan, we shall see how small is the saving in the amount of heat effected by the use of the vacuum pan.

Assume the mean temperature of the boiling liquor to be 220° Fahr., then

	Units of Heat.
54.000 lbs. raised from 160° Fahr. to 220° Fahr. =	about 6,480,000
24,000 lbs. water at 220° Fahr. converted into steam of the same temperature, at 960 units per pound, =	about 23,040,000
	29,520,000

which is only 14 per cent. more than that required by the first.

Boiling to Grain.—The liquor is drawn into the pan, at first high enough to cover the bottom worm and the jacket, if there be one. Steam is turned on, and the liquor boiled down rapidly till it begins to grow somewhat viscid, as shown by a drop or two removed from the pan by the "proof-stick" drawing out to a thread between the finger and thumb. The higher the proof (*i.e.*, the longer the thread) the "charge" is carried to, the larger will be the number of grains of sugar made when granulation does take place, and consequently the smaller will be the ultimate size of the grains after boiling the pan full—other things being the same. When the workman judges the proof (and this will vary with the degree of purity of the liquor he is using) to be right for the particular kind of grain he wishes to make, he lets the temperature of the mass rise somewhat, runs in a fresh portion of unboiled liquor, which disturbs the state of supersaturation in which the boiled liquor was, and induces the formation of more or less of sugar crystals. These first appear as little bright specks ("sparks") floating in the "proof," and afterwards rapidly increase in size. They are fed by the constant admission of fresh unthickened liquor till they attain the size wished, or till the pan is full. In the first case the admission of liquor is stopped, and the concentration continued to a degree of "stoutness" as great as is compatible with the subsequent working of the mass, which is then let entirely out of the pan. If the grain (crystal) has not attained the required size when the pan is full, a portion—say one-half or two-thirds—of the contents are let out, and then boiling resumed. The comparatively few crystals left in the pan now receive on their surfaces nearly all the sugar deposited from the fresh portions of liquor as they are evaporated, and consequently grow fast. This letting out ("cutting") is sometimes repeated seven or eight times, so that the final panful of very big crystals has been as much as twenty-four hours boiling.

The actual working of a pan, as applied to the boiling of various qualities of raw sugar and of syrups of varying degrees of exhaustion, can only be taught or learnt at the pan itself.

Whether large crystals or small have been made, their mother liquor must be separated from them. The most obvious and most simple way of doing this is to put the mass into a vessel in which it can drain. This is done in loaf-sugar making.

Loaf Sugar.—The granular magma of sugar crystals and syrup, which is a hot saturated solution of sugar *plus* the impurities of the raw, as it leaves the pan is received in heaters or jacketed pans, provided or not with mechanical stirrers, and brought to a temperature of about 180° to 190° Fahr. It is next filled out into a number of conical moulds, each holding from 7 to 12 lbs. of it, and allowed to stand for from twelve to twenty hours to cool. During this time the sugar held in solution in the syrup by virtue of the high temperature crystallizes out, and cements the existing grains of sugar firmly together.

The stopper which closed the hole in the apex of each mould is then removed, and a steel pricker is

* Reckoned from 0° Fahr.

driven up for a few inches into the solid mass of sugar; and the mould, with its contents, set to drain over a gutter of some kind, which will take the syrup away to a store tank.

The time required for the running off of the syrup will obviously vary with the viscidity of the syrup and with the degree of fineness of the grain; but with average goods—such as are made for the English market—twenty-four to thirty-six hours may be taken to be the time needed. However perfectly the sugar may drain, the crystals must remain wet with the syrup which bathed them ("green syrup"); and as that syrup was more or less coloured, the sugar, though white in itself, will appear yellow or brown.

Liquoring.—To remove the remainder of the green syrup it is necessary to displace it with a more colourless solution, which is effected by pouring on to the base of the loaf a clear saturated solution of pure sugar, which, as it sinks downwards, carries with and before it the green syrup. This "liquoring" is repeated till the sugar is quite white ("nett"); the loaf is allowed to drain as completely as possible; the portion of liquor retained in the "head" by capillary attraction is drawn off by help of a vacuum pump; the loaf "knocked out," papered, and set in a hot-air chamber (stove) at about 130° Fahr. to dry.

Crystal-making. — When large grain has been formed in the pan with the intention of selling the sugar as dry white crystals, the mass is filled out into the baskets of centrifugal machines, which consist essentially of a revolving perforated basket and sieve. The centrifugal force due to rotation forces the syrup through the perforation, while the solid grains of sugar are left behind.

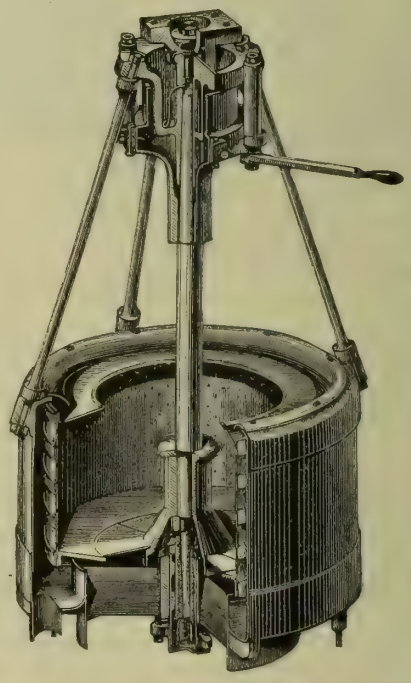
Centrifugals. — These invaluable machines take many forms, and as some are better adapted than others for particular work, it is, perhaps, worth while to more particularly describe some of the latest improvements. In the form most commonly used in English refineries a vertical axle spindle, driven by a pulley at its lower end, runs in two brasses, one at its extreme lower end, and another coned and widest at the top, which takes the upper coned end of the spindle, and consequently carries the weight of the basket which is fixed to the extreme upper end. No lateral motion of the basket is here possible without the axle makes room for itself by destroying the upper cone brass, and any irregularity of loading the sieve causes a great deal of vibration, which has to be taken up by heavy and solid foundations. These machines are, therefore, not well adapted for putting on upper floors. The best form of this type of machine is that of Messrs. Manlove & Alliott.

The most common form of another type are the machines made by Fesca of Berlin. Here the spindle, which is very long, rests on a steel button at its lowest end, while the upper brass, which is not more than half-way up, is not rigidly fixed, but is simply held in its place by six tie rods coming from the casing of the machine, and each provided with a powerful india-rubber compression spring or buffer at its outer end. This arrangement allows of a little controlled and restricted motion of the spindle and the basket fixed to it, in a lateral direction, so that the basket can revolve round its real centre of gravity even when loaded to some extent unevenly. This machine, which is almost universally used in Germany, and latterly to a considerable extent in England, may be put on any floor of a house, as it requires no foundation, but only a *loose* frame of timber to bolt it to.

Another form of machine, which allows of the self-balancing of the irregularly weighted basket in perhaps a more perfect manner, is Weston's centrifugal, as made by Mirrlees, Tait, & Watson, of Glasgow.

Hepworth's centrifugal machine (Manlove & Alliott), Fig. 8, differs from the last in having the casing suspended and the basket spindle fixed to it,

Fig. 8.



so that the swing produced by irregular loading is shared by both basket and casing, and the former can never hit the latter, and so produce an accident, even in the most extreme case.

The sugar grains left in the sieve of the centrifugal are cleansed either by dashing water or colourless syrup on them—which, as it forces its way through under the influence of the centrifugal force, takes with it most of the coloured syrup—or by partially condensed steam. The mode of use of this last will be discussed separately at the end of this section.

The syrup from the first crop of sugar (crystals or loaves) is reboiled either with or without previous refiltration over char, and when "spun," gives pure sugar grains coated with a syrup containing the

concentrated impurities of the original liquor. The reboiling of the successive syrups is continued till the last left is so poor in sugar that it will not readily crystallize in the vacuum. When this point is reached the syrup is simply concentrated pretty highly in the vacuum pan and let out into vessels, in which it can stand and cool for a week or so to crystallize. The syrup obtained from this last crop of crystals is reheated to dissolve floating grains of sugar, slightly concentrated, if necessary, and sold as treacle.

The above does not, of course, represent the routine in all houses. In some, as in those on the Clyde, it is the custom to melt fresh raw sugar of lower qualities with the syrup from the sugar made from fine raw, &c.

Special Processes—Cleaning Raw Sugar.—For the manufacture of the finest class of refiners' goods certain raw sugars, especially low "beets," are wholly unfit, either on account of the excessive quantity of syrup adhering to the grains, or to the peculiarly harmful nature of that syrup. Accordingly, many attempts have been made to devise a simple and economical means of separating sugar and syrup before melting the former. In principle all proposed methods are alike. The syrup on the grains is more or less diluted and warmed to render it fluid, and is then removed more or less completely from the grains by mechanical force, applied sometimes by pressure of screws or weights (given up), sometimes by exhaustion of the air from below a false perforated bottom on which the moist sugar rests (not practically in use—force is not sufficient in most cases), but generally and largely by the centrifugal machine. The particular ways of warming and moistening the raw sugar have been made the subjects of many patents from the time of Lord Howard de Walden, who in 1853 anticipated all that has been done since in this direction, and the publication of whose specification ought to have prevented the granting of any more patents for steaming sugar in centrifugal machines.

Weinrich Process.—One form of this cleansing by steam has been patented in this country by Moritz Weinrich, and is now largely in use. The sugar to be cleaned—which must have a fair grain and be free from syrupy lumps—is packed dry by hand into the annular space between the sieve of a centrifugal, having a removable top ring and a loose central metal ring. The top ring of the sieve is bolted on, and the machine set in motion. The centrifugal force compresses the sugar against the face of the sieve, and holds it there, while the central ring is simply lifted out by hand. A blast of low-pressure steam, mixed with a large quantity of cold air, to partly condense it to a wet fog, is then admitted through an opening in the cover of the centrifugal, and maintained until the warm wet mist ceases to cause a highly-coloured syrup to run from the machine. The sugar remaining in the sieve is hard and dry, and is removed by tools after taking off the top ring of the sieve.

Boivin and Loiseau's Process.—In the refineries of M. Sommier at Paris, and in those of Messrs. Tate and Sons of Liverpool and London, a process, invented by MM. Boivin and Loiseau, is in use for the purification of raw sugar, which is a modification of the ordinary double carbonation of the beet-root factories. One portion of the sugar to be treated is dissolved up to about 20° B. thick (or the wash waters, bag washings, &c., are used here), and mixed with so much lime as is equal to about 20 per cent. of the sugar, and the mixture cooled to a temperature not exceeding 30° C. Carbonic acid, obtained from a lime kiln in the usual way, is then pumped through the *cold* alkaline solution, which after a certain time begins to get somewhat less fluid, and then almost suddenly assumes the appearance of an opalescent, gelatinized paste. MM. Boivin and Loiseau say that this is caused by the formation of "hydro-sucro-carbonate of lime," but no body having a definite composition has as yet been obtained to justify the name. The paste or jelly is mixed with the rest of the sugar to be treated, and the whole boiled up. This causes the precipitation of a large portion of the lime as carbonate, which carries down with it, as usual, a considerable amount of the organic, non-saccharine impurities of the liquor. Another portion of the lime is left in solution, and after separation of the first precipitate by filtration, is precipitated in its turn by another dose of carbonic acid while hot. Because of the lime which remains in solution uncombined with carbonic acid, when the liquid is heated, any glucose which is present is destroyed as such, and converted into certain weak and ill-defined acids, which remain in solution combined with lime, and are subsequently partly precipitated on the second carbonation. This process has been adopted and applied by Tooth to the working of cane-juice.

Langen Process.—Herr Eugen Langen of Cologne has worked out a rapid method of preparing loaf-sugar from the *masse-cuite*, which will no doubt come into extensive use in time. He fills the hot magma of crystal and syrup into moulds, which are segments of a ring which would fit a given centrifugal machine, and which can be closed on the wider face. When the mass is cold and set, the covers are removed, and the moulds, to the number of ten to thirty, as the case may be, are set in the centrifugal, and "spun" till all the "green syrup" is out. They are next set—narrow face first—over openings through which "fine liquor" can be forced, and a joint is made by clamping each mould down on an india-rubber washer. "Liquor" is given till it runs clear from the outer (wider) face, the moulds and contents are returned to the centrifugal machines, and the excess of "fine liquor" spun out, carrying with it the last adhering green syrup. The sugar then only requires drying by some appropriate means. Langen divides his moulds by a number of movable plates, so that the sugar obtained is in the form of slabs about an inch thick, which admit of rapid drying by forcing hot, dry air through the mould containing them after removal of the dividing plates. The process, as a

whole, is patented in Great Britain and worked by two firms.

Moulding Sugar.—Great numbers of patents have been taken out from time to time for methods or apparatus for moulding moist, white, granular sugar as it leaves the centrifugal machine after a severe washing or steaming, or both, into solid blocks of various size in imitation of ordinary loaf-sugar. None of these machines had any practical value until MM. KOHRIG and PZILLAS brought out their ingenious press. In this machine a brass cylinder (about seven-eighths of an inch thick), having eighteen rectangular slots cut through it, is caused to move round on the face of a half ring of stout brass disposed inside it, and supported by fixed points, in a series of eighteen steps or separate motions. Each slot, when over the internal half ring, forms a mould into which moist sugar is fed by spiked rollers from a hopper resting on the upper part of the cylinder. As each mould containing the loose sugar is pulled round into the horizontal plane of the cylinder, a stamper, driven by an excentric, comes up and compresses its contents about one-sixth. The compressed sugar in the moulds is driven out on the other side of the cylinder on to boards placed to receive it, by a second stamper acting from the inside of the cylinder. Without detailed drawings it would be impossible to give a clear idea of the machine, or the ingenuity of the various contrivances which render it such a great practical success. The sticks of sugar are carried on the boards on which the machine places them to drying chambers, where they become as hard as ordinary loaf-sugar, and are subsequently cut up into tablets similar to those commonly seen at cafés in Paris and elsewhere.

Production and Consumption of Sugar.—RUEB and LEDEBOER have calculated the production of sugar for the whole world to be as follows; but from this estimate they have omitted China and India, which both produce large quantities, and export no inconsiderable amount:—

	1853.	1863.	1872.
	Tons.	Tons.	Tons.
Java and Madeira,...	100,000	125,287	207,842
Surinam,.....	16,520	13,683	12,291
Cuba,.....	322,025	506,860	711,795
Manilla,.....	40,000	83,151	91,701
Porto-Rico,.....	111,975	63,000	89,559
Brazil,.....	138,000	238,280	157,809
Mauritius,.....	80,811	158,209	124,806
English Antilles,....	61,000	13,894	21,279
Natal,.....	—	1,317	8,878
Jamaica,.....	21,361	28,444	26,296
Barbadoes,.....	25,556	29,583	37,762
Trinidad,.....	24,010	37,421	60,023
British Guiana,.....	38,096	53,974	73,556
Australia,.....	2,485	2,988	4,920
Louisiana,.....	224,662	—	69,800
Martinique,.....	20,700	30,459	39,699
Guadaloupe,.....	14,800	30,266	31,786
Reunion,.....	33,100	68,616	30,450
Cayenne,.....	300	420	324
Egypt,.....	1,303	341	20,359
Europe,.....	200,000	452,129	1,142,896

The consumption of sugar in the different countries of the world has been estimated as follows:—

Country.	Tons.	Population.	Lbs. per Head.
Great Britain,.....	900,000	31,629,300	62·5
Germany,.....	315,000	42,756,900	16·1
France,.....	275,000	36,377,600	16·6
Russia,.....	250,000	82,135,700	6·7
Austria,.....	170,000	20,395,000	18·3
Spain,.....	50,000	16,385,500	6 4
Belgium,.....	50,000	4,827,800	22·7
Holland,.....	30,000	3,579,400	18·4
Turkey,.....	25,000	23,610,000	2·3
Sweden and Norway,	20,000	4,870,300	7·4
Portugal,.....	15,000	4,324,000	7·4
Denmark,.....	15,000	1,785,000	18·2
Switzerland,.....	11,000	2,650,600	9·0
Greece,.....	3,000	1,457,100	4·6
Europe,.....	2,129,000	287,243,200	16·8
United States,.....	750,000	38,925,000	42·3
English Colonies not producing sugar,..	200,000	7,000,000	64·0
Total,.....	3,079,000	324,168,200	20·9

In preparing the foregoing pages the writer has made free use of the stores of information collected in the works cited below, which he can strongly recommend to the attention of those practically interested in the question of sugar.

Considerations of space have compelled the omission of much that would have been both interesting and useful to those who have no acquaintance with the subject, and who might wish to render themselves familiar with all parts of it—*e.g.*: The construction of the vacuum pan, the air-pump, and the condenser for working it; the analyses of various raw and refined sugars and molasses; abstracts of patents relating to sugar, &c. But to go into detail on all points of interest would necessitate the production of many thick volumes.

There is no good book on sugar in English. The volumes of the "Sugar Cane" contain several valuable papers, and should be consulted.

STAMMER'S "Traité complet de la Fabrication du Sucre," published in French and German (the German edition is best); very good.

WALKHOFF'S "Der Praktische Rübenzucker Fabrekant und Raffinadeur," also published both in French and German; good, but not so recent.

The sixteen volumes of STAMMER'S "Jahresbericht über die Untersuchungen und Fortschritte auf dem Gesammtgebiete der Zuckerfabrication;" most useful.

The twenty-eight volumes of the "Zeitschrift des Vereins für die Rübenzucker-Industrie des Deutschen Reichs."

When the two last-named periodicals are not easily to be obtained, DINGLER'S *Polytechnical Journal*, which is to be found in most Chemical Libraries, and in some of the Patent Offices, should be searched for the many important papers and abstracts which it contains.

SULPHUR.—*Brimstone. Soufre*, French; *Schwefel*, German; *Zolfo* or *Solfo*, Italian; *Azufre*, Spanish. Atomic weight, 32. Symbol, S. Vapour density 32, hydrogen 1; or 2·218 air, 1.

Sulphur is a pale yellow solid, very brittle, becoming electrical by heat or friction. It was at one

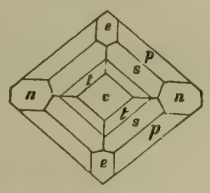
time used as a source of electricity, being formed into globes and cylinders, and mounted as glass cylinders and plates are at the present day.

It crystallizes in two distinct systems. Native sulphur is found crystallized in the rhombic system. The simplest form is that of a double pyramid, with a rhombic base (Fig. 1). Fig. 2 (Naumann) shows

Fig. 1.



Fig. 2.



the horizontal projection of a complicated crystal, where *p*, *s*, and *t* are the faces of pyramids of various degrees of acuteness; *e e*, faces of the macrodoma; and *n n*, of the brachydoma, *c* being the terminal plane.

The specific gravity of sulphur in the native crystalline state is 2·05. It is insoluble in water, but bisulphide of carbon dissolves it readily, as do oil of turpentine, benzine, and petroleum. The crystals left by the evaporation of a solution of sulphur in bisulphide of carbon are similar to those found in nature. It begins to melt at 238° Fahr. (114°·5 C.) (Brodie), and at 248° Fahr. (120° C.) becomes a thin, brownish-yellow, transparent liquid. If now cooled, a transparent mass is formed, which gradually becomes opaque. On heating still further, a very perceptible change takes place. The sulphur, instead of remaining in the liquid state, becomes of so thick a consistence, that the vessel containing it may be inverted without loss. This occurs at a temperature of between 428° and 482° Fahr. (200° to 250° C.). At a still higher temperature the action is reversed; the melted sulphur becomes thinner and thinner, until it reaches its boiling point at 824° Fahr. (440° C.), when it begins to pass off as an orange-coloured vapour. The density of this vapour at 1000° C. is 32, hydrogen being taken as unity.

Other phenomena may be noticed by interrupting the experiment at various stages. For instance, if it be wished to obtain crystals of sulphur, it is only necessary to take the sulphur while in the first liquid stage, to pour this into a basin or other vessel with sloping sides, and there allow it to stand. In a few minutes after the top portion has solidified and formed a crust, two holes are broken through this crust at opposite sides of the vessel. If the basin be now inverted partially, the sulphur, which still remains in the liquid state in the interior, will run out of one hole while air rushes through the other. The vessel is allowed to stand until cold, when, on dividing the solidified mass by means of a saw, it will be found to be full of beautiful crystals of sulphur. These crystals belong to the oblique prismatic system, and have a lower specific gravity —viz., 1·982—than that of the first-named variety.

If the sulphur, immediately after passing, or perhaps better, while scarcely through the thick stage, be poured into water, it does not solidify and assume the ordinary yellow brittle appearance which it would do were it so treated while in the first liquid state; instead of doing so it remains in the plastic condition even when cold. In this state it is perfectly elastic, may be pulled out to a considerable length without breaking, and, in fact, does not in the remotest degree resemble sulphur. But for its colour, it might be mistaken for wheat gluten, possessing the same soft elasticity as that body. It will remain in this state for a short period, but resumes its ordinary aspect after the lapse of some days.

Another variety is obtained by precipitating alkaline polysulphides by an acid. The so-called *milk of sulphur* is formed; it has a greenish-white colour. It is amorphous, but soluble in bisulphide of carbon.

Lastly, there is a variety known as amorphous insoluble sulphur, which may be obtained by decomposing disulphide of chlorine, Cl_2S_2, by water. It is yellow in colour, amorphous, and insoluble in bisulphide of carbon.

To recapitulate, therefore, we have the following varieties:—

1. Octahedral sulphur.
2. Prismatic sulphur.
3. Plastic sulphur.
4. Amorphous soluble sulphur.
5. Amorphous insoluble sulphur.

Occurrence.—It is found in nature both in the free state, as native sulphur, and in combination in sulphides and sulphates. Sulphur forms a constituent of some vegetable and animal compounds.

Native sulphur is found in two very different ways:—1st, in volcanic districts, where it is often being deposited at the present day by active volcanoes; and 2nd, interbedded with limestone, shale, and gypsum in Tertiary rocks.

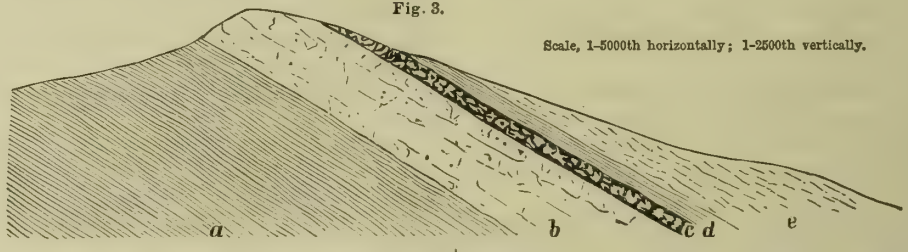
Solfataras are old craters, showing no other sign of volcanic activity than sending out sulphurous and other vapours from holes called *fumaroli*. The sulphur is deposited in cavities in the rock or at the surface, mainly from the oxidation of the sulphuretted hydrogen in the vapours, thus — $H_2S + O = H_2O + S$; and partly by the action of sulphur dioxide on sulphuretted hydrogen, thus —$2H_2S + SO_2 = 2H_2O + 3S$. The result of this action is that the earth in the neighbourhood of a *fumarole* becomes sufficiently impregnated with sulphur to render it a useful source of this element. The deposition of sulphur is sometimes increased by building large chambers over the *fumaroli*, and so condensing much of the vapour which would otherwise have escaped.

Not only is sulphur found in these solfataras, or semi-spent volcanoes, but it is deposited also in a similar manner by some active volcanoes; and, again, deposits are found in craters which show no sign of activity. "Some spent volcanoes, which have probably long existed in the condition of so-called solfataras, abound in massive deposits of pure

sulphur—*e.g.*, some of craters of Lipari, of Iceland, of Java, of Quito, &c." (Scrope's "Volcanoes," 1872, p. 143). The most celebrated solfatara is that near Pozzuoli, in the Bay of Naples, which has attracted attention in all ages, and where small quantities of sulphur are still being extracted. Mines are worked on similar deposits at Latera, in the province of Viterbo, Italy. At Krisuvik, in the south-west of Iceland, and also near Lake Myvatn, in the northern part of the island, sulphur is being deposited in considerable quantities over a large area by *fumaroli* ("Sulphur Deposits of Krisuvik," Chas. W. Vincent; *Soc. Arts Journal*, vol. xxi., 1873, p. 137; and "Sulphur in Iceland," by C. Carter Blake, London, 1874). The crater of the Peak of Teneriffe is an immense solfatara (Von Buch). Sulphur is obtained from the volcano Popocatepetl, in Mexico; from solfataras in Guadaloupe and Japan. In descriptions of the now famous Yellowstone region of the Rocky Mountains, which resembles and excels Iceland in its geysers, we find frequent mention of deposits of sulphur formed by springs and "steam vents"—*i.e.*, *fumaroli*.

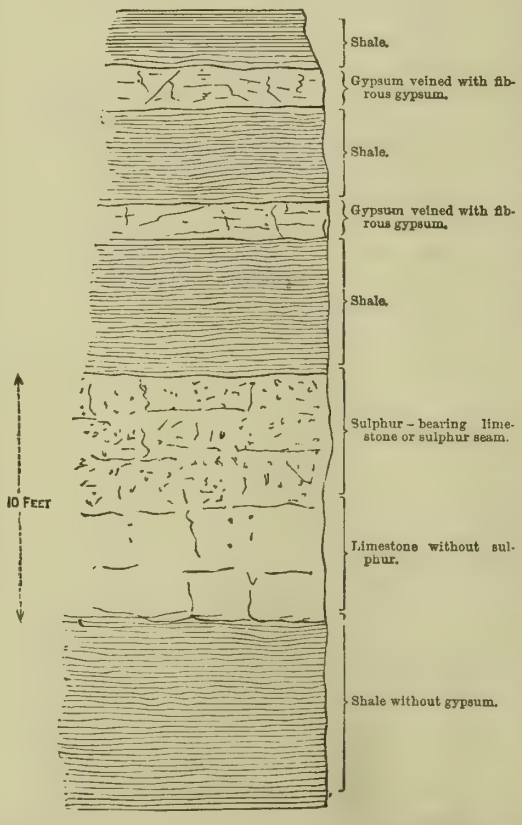
Sulphur Occurring in Sedimentary Rocks.—It is in this way that sulphur is found in Sicily, the Romagna, Croatia, Galicia, and Poland. The sulphur district

Fig. 3.



of Sicily is contained in the provinces of Caltanissetta and Girgenti, and part of that of Catania; and

Fig. 4.



there are two isolated patches of sulphur-bearing rocks at Lercara, in the province of Palermo, and Gibellina, in that of Trapani.

The sulphur occurs interbedded with rocks of Tertiary age. The exact horizon is in the Upper Miocene, the beds of which, judging from their fossil contents, appear to have been deposited in lakes. The sulphur rock itself is a slightly marly limestone, associated with sulphur. Sometimes the sulphur is disseminated through the limestone; in other cases there are thin alternate layers of limestone and sulphur. The number of seams of sulphur rock varies according to the locality. The seams are separated by partings of black marl, from 20 inches to 6 feet thick, and some of the seams attain a thickness of 28 feet. The total thickness of all the sulphur seams put together in one case reaches 100 feet; but the average thickness of the sulphur-bearing limestone is only 10 or 12 feet, and the ore contains, on an average, 20 to 21 per cent. of sulphur.

At their outcrop the seams are thoroughly decomposed; the sulphur, in presence of calcic carbonate, oxygen, and moisture, becomes oxidised, and produces sulphuric acid, which decomposes the limestone and forms gypsum. No sulphur therefore is seen at the surface; but you have a whitish, earthy, friable rock, the *briscale* of the Sicilian miner. The occurrence of this *briscale* is a sure indication of the existence of a sulphur seam; it is to a sulphur seam what the *gossan* is to a lode or mineral vein.

The sulphur limestone was probably deposited in the lakes by the decomposition of calcium sulphide, brought down by springs. For details about the occurrence of sulphur in Sicily, and the various theories concerning its origin, the reader is referred to a memoir by Mottura,* entitled "Sulla formazi-

* For a short abstract of Mottura's memoir see *Journal of the Society of Arts*, vol. xxi. p. 169, January, 1873. See also article in the *Annales des Mines*, 7e Série. Tome vii., 1875, pp. 1–84. It contains much matter taken from memoirs by Mottura, and from Parodi's work, "Sull' estrazione dello Solfo in Sicilia," Firenze, 1873.

one terziaria nella zona solfifera della Sicilia," "Memorie del R. Comitato Geologico d'Italia," vol. i., 1871. Fig. 3 is a cross-section of La Crasta Sulphur Mine near Delia, copied from Mottura's work, and shows how the seam of sulphur lies: *a*, ferruginous marls and clays (Lower Miocene); *b*, siliceous limestone (Upper Miocene); *c*, sulphur seam, decomposed into *briscale* at the outcrop; *d*, gypseous and bituminous marls; *e*, marly limestone with foraminifera.

In the Romagna there are some large and important mines near the town of Cesena. The geological horizon is the same as that of the Sicilian sulphur. There is a bed of limestone about 10 feet thick, part or the whole of which is sulphur-bearing. The accompanying section (Fig. 4), showing the rocks near the sulphur seam in one of the Boratella mines, gives a good general idea of the mode of occurrence.

At Radoboi, in Croatia, "the sulphur is intercalated in beds full of remains of insects and plants, and coloured brown by mineral resin and carbonaceous matter" ("Manual of Geology:" Jukes and Geikie, 1872, p. 55). At Swoszowice, in Galicia, the sulphur is found irregularly deposited in nests in shale, interbedded and veined with gypsum, and is worked at three horizons. The sulphur ore yields about 10 per cent. of sulphur ("Denkbuch des Osterreichischen Berg und Hüttenwesens," Vienna, 1873, p. 261).

Sulphur Mining.—In Sicily the sulphur seams are usually reached by means of inclined shafts, at angles of from 30° to 50°, which the miners ascend by steps cut in the rocks. The miners then drive out galleries 5 or 6 yards apart down the dip, and then galleries along the strike, leaving pillars 5 or 6 yards square. The galleries are 6 to 8 feet wide. The pillars are then gradually worked away, the roof being allowed to fall in. When there are two beds, one above the other, the pillars are supposed to be left one above the other; but from absence of plans, it very often happens that a pillar has a very unsafe footing. In many cases, however, especially where there are very thick deposits, the workings are most irregular; galleries are driven out in all directions, huge caverns of all shapes and sizes are excavated, and are kept up by an occasional small pillar, which often rests on the roof of a cavern underneath. The consequence is that after a time the workings fall in. The miners then make a fresh start somewhere else; and after a time, when they think the ground has got settled, go back into the old workings, driving in levels, which are secured by masonry all round. They then extract as much sulphur as they can.

The sulphur rock is worked away partly by the pick and partly by blasting. The state of mining in Sicily is so primitive that the ore is generally carried along the levels and up the shafts on the backs of boys and lads. The mines are drained by adit levels, hand pumps, and rarely by pumps driven by steam engines.

In the Romagna the system of mining is not so rude as in Sicily. At the Boratella mine, for instance, they sink shafts till they reach the seam, drive out levels, and then take away the sulphur seam, leaving pillars, 10 or 12 feet square, at distances of about 24 feet apart; the pillars gradually crumble away, and the roof falls. The mineral is conveyed underground by wheel-barrows and tramways, and is raised to the surface by horse-whims, or winding apparatus driven by a steam engine. The mines are worked at a depth of from 60 to 70 fathoms. When sulphur is worked in solfataras, the earth is simply dug up.

Natural Compounds of Sulphur. — Sulphuretted hydrogen is given off from volcanoes and solfataras, some mineral springs, such as the well-known one at Harrogate, and is found in the air of sulphur mines and in some coal mines. Sulphides of the metals of the alkalies and alkaline earths are also constituents of some mineral waters—such as those of Aix-la-Chapelle, Aix in Savoy, Saint Boës, near Dax, and Bex, in Switzerland—which afford evidence of the deposition of sulphur from aqueous solutions ("Manual of Geology," Jukes and Geikie, 1872, p. 55).

The sulphides of the heavier metals are so numerous that it will be impossible in the limits of this article to enumerate more than a few of them.

Iron pyrites, FeS_2, crystallizes in the cubical system; colour, between a brass-yellow and a gold-yellow. It is a mineral very largely diffused in nature, and occurs in a great variety of rocks of all ages.

Marcasite has the same chemical composition as iron pyrites, but crystallizes in the rhombic system, and has a much lighter colour. Like iron pyrites, it is used for making sulphur, sulphuric acid, green vitriol, and alum.

Pyrrhotine, or magnetic iron pyrites, Fe_7S_8, has a peculiar bronze colour. It is sometimes important as containing a few per cent. of nickel.

Mispickel, $FeAs + FeS_2$, is useful as a source of arsenic.

Among other important sulphides which constitute valuable ores of the respective metals are Zinc-blende, ZnS; Copper-glance, Cu_2S; Bornite, $3Cu_2S + Fe_2S_3$; Copper-pyrites, $Cu_2S + Fe_2S_3$; Galena, PbS; Cinnabar, HgS.

Silver-glance is a sulphide of silver, Ag_2S, and there are numerous sulpho-arsenides and sulpho-antimonides of silver—such as proustite, pyrargyrite, stephanite, and polybasite.

Sulphur occurs also in nature in sulphates. In mineral springs, for instance, there are sulphates of the alkalies, such as sodium sulphate. The sulphates of the metals of the alkaline earths are widely distributed. Barytes, or barium sulphate, is very common in mineral veins; gypsum, $CaSO_4 + 2H_2O$, is found in large quantities in sedimentary rocks. The sea forms a vast reservoir of sulphates, containing, as it does, 0·162, or, roughly speaking, one-sixth, per cent. of gypsum, and 0·197 or nearly one-fifth per cent. of sulphate of magnesium (Epsom salt). Natural alums, or hydrated double sulphates of aluminium, and another metal—such as potassium, sodium, magnesium, or iron—are also met with.

Sulphates of zinc, cobalt, iron, copper, and lead are minerals found in nature, and have no doubt all been produced by the oxidation of the sulphides of these metals.

In the vegetable kingdom some of the essential oils—such as oil of mustard, oil of garlic, and oil of assafœtida—contain sulphur.

Among the components of animal substances containing sulphur may be mentioned the proteoids or albuminoids; the blackening of a silver spoon by a boiled egg is a familiar illustration of the fact. Fibrin, whether of blood or flesh, also contains more than 1 per cent. of sulphur; and sulphur enters into the composition of casein, protein, hæmatocrystallin, and globulin, as well as of hair, horn, nails, and feathers. Enough has therefore been said to prove that sulphur is a very widely distributed element, in the animal, vegetable, or mineral kingdoms.

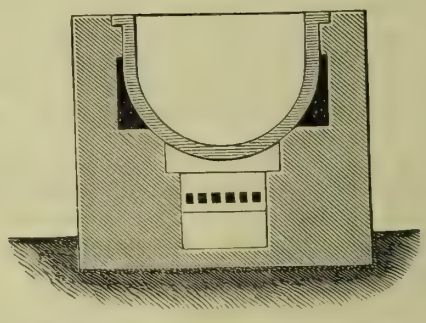
Uses of Sulphur.—Sulphur is used in making sulphuric acid, sulphurous acid, and many of the compounds of sulphur, such as hyposulphite of soda, bisulphide of carbon, artificial vermilion, &c. It is one of the constituents of gunpowder, and is used in the manufacture of lucifer matches. Large quantities of sulphur in powder are used in Italy, France, and Spain, for sprinkling vines as a preservative against the disease known as oïdium. Sulphur is used for hops in the same way. Some is used in medicine, and it is finally employed as a cement, and for taking casts of coins, medals, &c.

Direct Extraction of Sulphur from Sulphurous Earths.—This extraction may be performed in various ways:—

1. Melting in pans.
2. Liquation in iron cylinders.
3. Distillation in earthen pots.
4. Liquation in small kilns (*calcarelle*).
5. Liquation in large kilns (*calcaroni*).
6. Distillation in iron retorts (*doppioni*).
7. Liquation by means of steam.
8. Extraction by bisulphide of carbon.
9. Processes of Hirzel, Gill, and Kayser.*

1. *Melting in Pans.*—This method has been employed for rich sulphur ore, and stuff that is in too fine a powder to be treated conveniently by liquation in kilns. The accompanying Fig. 5 † shows the kind of pan that was used at Lercara in Sicily. The ore was thrown into the pans little by little, and as it melted, the workman drew out the earthy particles which settled at the bottom. A high heat is not advantageous. This may be inferred from what has been said before respecting the changes which take place during the fusion of sulphur at different temperatures. For the purpose of purification the lowest heat consistent with perfect fusion had to be employed. The liquid sulphur was thus in its thinnest state, easily allowing the earthy particles to subside. When the pan was full of melted sulphur the workman allowed it to settle a little, and then ladled out the sulphur into moulds. The two or

Fig. 5.

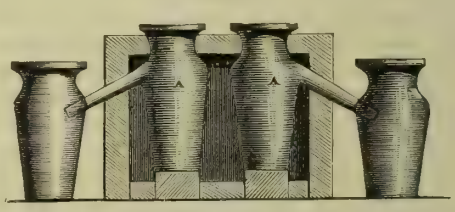


three last ladles were very impure, and had to be treated in the kilns together with the residues of the operation, which still retained a considerable quantity of sulphur.

2. *Liquation in Iron Cylinders.*—This was a method in use at one time in places in Sicily. The sulphur earth was heated by means of a wood fire in iron cylinders inclined towards the front. The cylinders, containing each some 4 tons of ore, were closed during the operations, and there was thus little loss from sublimation or oxidation. However, much sulphur remained in the residues, and the cast iron was rapidly corroded. At Swoszowice, near Cracow, the process adopted is partly liquation, partly distillation. The ore is heated in cast-iron sloping tubes, each of which holds rather more than 1 cwt. of mineral. Some sulphur is collected by tapping it off at the lower end of the tube, and the rest is obtained by the condensation of the vapours that escape. For figures and description, see "Berg und Hüttenmännische Zeitung," 1861, pp. 1–15, and "Metallurgy," by Crookes and Röhrig, p. 710.

3. *Distillation in Earthen Pots.*—This system, though never used in Sicily, has been employed in the Romagna, and may still be seen at the Solfatara, near Naples, though the production is very small indeed. A A are two earthen jars standing upon a

Fig. 6.



raised support of bricks. The mouths of these jars protrude slightly over the top of the furnace. This is for the purpose of allowing the operator to fill in the charge and remove the earthy residuum. A hollow tube or arm projects laterally and slightly downwards from each of the pots or retorts, which arm is thrust into another pot or vessel to receive the sublimed sulphur which condenses in it. When the subliming pot has received its charge the lid

* Described by Parodi; they are of no commercial importance, and need not be further noticed here.

† Copied from Parodi's figure in his work, "Sull' estrazione dello Solfo in Sicilia" Florence, 1873.

is luted on and the furnace lighted. As each pot becomes heated the various changes of fusion take place, and at last sublimation begins. The vapour then passes over into the condensing jar. All the earthy matter is left in the retort-pot, and is removed previous to the introduction of another charge.

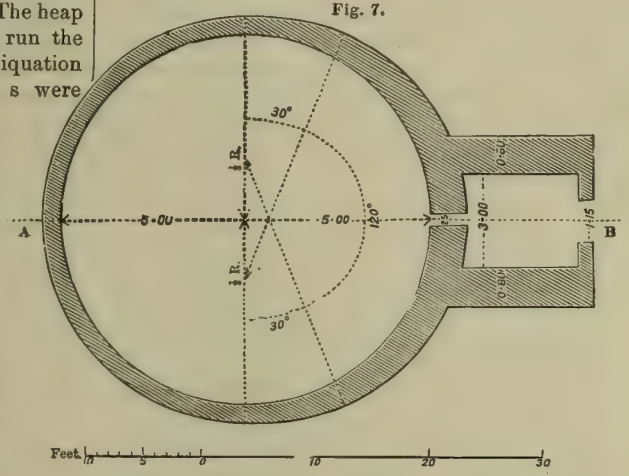
4. *Liquation in Small Kilns* (*Calcarelle*).—The *calcarelle* are simply small *calcaroni*, which will be described immediately. The heap of mineral was about 6 to 7 feet in diameter, with an average depth of 16 inches, and contained about 4 tons. The heap was lit in the evening; sulphur began to run the next morning, and towards evening the liquation was finished. The next day the residues were removed, and the refilling commenced. About one-third of the sulphur contained in the ore was obtained, and the rest lost as SO_2, which did great damage to fields in the neighbourhood. Nearly all the Sicilian sulphur was obtained by means of calcarelle up to the year 1850.

5. *Liquation in Large Kilns* (*Calcaroni*).—These are a great improvement on the smaller ones. A *calcarone* (or *calcherone*) is a great heap of sulphur ore inclosed in a kiln, and a part of the sulphur is burnt in order to produce the heat necessary to fuse the remainder.

The kiln* is an elliptical or circular pit, lined with masonry, and having the bottom strongly inclined towards the front. The angle varies from 10° to 15°, and the proportion between the average depth of the pit and its diameter is from one-fourth to one-fifth. The kilns are generally built on the side of a hill, and advantage is then taken of the form of the ground to avoid unnecessary excavation and have convenience for charging and discharging. In front of the kiln is left a rectangular opening 4 feet high by 10 inches wide, called the *morte*. The interior of the kiln is carefully plastered, so as to present a smooth surface impermeable to the fused sulphur. The bottom of the kiln is formed of fine residues, locally called *ginese*, beaten down quite hard, and reposing either on the natural soil, or better, on brick-work. In some districts the *calcaroni* are not built exactly as shown in the figure, with a wall all round. At Racalmuto, for instance, there is only a breast wall in front. The reason of this is probably that the Racalmuto ores require more air. Fig. 7 is the plan of a calcarone; the dimensions given are in metres and centimetres. Fig. 8 is the section along A B.

In charging the kiln large pieces of ore are first put on the bottom, and the large pieces continued in the centre, and smaller stuff outside. The *morte* is surrounded by large blocks of sterile rock. The charging is continued till the top edge of the kiln is reached; and in proceeding upwards three to five chimneys, built with large lumps, are left, and these are generally placed in the back part of the kiln. The height to which the ore is piled varies with the diameter of the calcarone. The unit of measure in speaking of the size of a calcarone, and of sulphur ore generally, is the *cassa*, which varies considerably in different localities, indeed from $2\frac{1}{2}$ to 6·4 cubic metres. On an average the *cassa* may be taken at about $3\frac{1}{4}$ cubic metres ($4\frac{1}{4}$ cubic yards), which

Fig. 7.



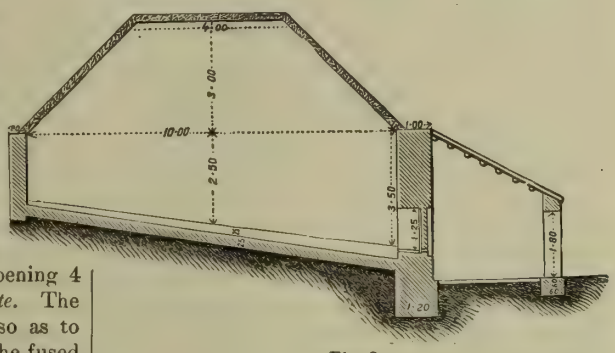


Fig. 8.

corresponds to rather more than 4 tons of sulphur ore.

Calcaroni vary considerably in size; very small ones will contain 10 *casse*, others 20, 50, 100, 200, and even up to 1000 *casse*. One cause of the variation in size is the length of time liquations can be carried on. If liquations can be performed all the year round small *calcaroni* are used; but if, from fear of damage to growing crops, the miners have only the right to work their *calcaroni* during certain months of the year, larger ones must be employed. The size of the *calcaroni* depends also on the quality of the ore.

The charging completed, the surface of the truncated cone of ore is covered with a layer of fine residues derived from the preceding operations; the *morte* is closed by a thin wall with a few holes at various heights, which are luted up with clay. Everything is now ready for beginning, and the

* The following description of the calcarone process is mainly taken from Signor PARODI'S very valuable work, already mentioned, on the "Extraction of Sulphur in Sicily."

calcarone is lighted by throwing into the above-mentioned chimneys lighted wisps of straw dipped in sulphur. At Racalmuto, where these chimneys are not used because they are found to be detrimental, the heap is lighted at the back. The burning is allowed to go on for a few hours, and then every hole is closed and the calcarone left to itself.

Seven or eight days after lighting, the first fumes of sulphurous acid, mixed with aqueous vapour, appear, and small deposits of sublimed sulphur begin to form near the top of the chimneys, which are closed again with fresh residues. The kiln is now watched more attentively, and particular care is taken to keep the *morte* the coolest part of the *calcarone;* the shape of the heap, and lighting it from behind, so that the heat propagates itself from the back to the front, help to effect this object. The sulphur, finding its way along the bottom, always traverses a mass that is relatively cool and does not burn; and when the fire arrives at the *morte* all the rest of the ore has already given up its sulphur, and the operation is completed. The first sulphur that runs down, finding the *morte* completely cold, solidifies, and has to be melted by opening the *morte* in part and throwing in lighted bunches of straw. When the solidified mass has thus been removed the *morte* is built up again, and remains hot enough to prevent further difficulties. When the average temperature of the kiln is too low the sulphur solidifies on coming to the *doors*, *i.e.*, the lumps of sterile rock round the *morte*, and closes them up altogether. The calcarone is then said to be *choked.* This difficulty is graver than the preceding one, as the workmen cannot reach in to the *doors* with bundles of straw; and if the remedy is delayed the sulphur accumulates behind the doors and comes in contact with lighted mineral, burns, the heat in the calcarone rises rapidly, and the sulphur passes into the viscous state, and ceases to run, or is volatilized, causing very great loss. The remedy for this *choking* consists in opening the *morte* and uncovering the front part of the heap. This causes a strong draught, and the combustion near the *doors* is rendered more active.

When by means of the little holes in the *morte* it is ascertained that there is a quantity of melted sulphur in it, a hole is made at the bottom of the calcarone, and the sulphur is allowed to run out. Sometimes the sulphur is allowed to run out continuously; in other cases there are two or three tappings in the twenty-four hours, and in the intervals the liquid sulphur collects in the *morte.* The sulphur is cast in wooden moulds, which are moistened with water to prevent adherence, and the lumps or cakes, weighing about 1 cwt., are known as *balate.*

The end of the operation is announced by the *morte* taking fire, and the change in the quantity of the sulphur. The calcarone works hot towards the end, and the sulphur takes up impurities, which it finds near the *morte.*

The duration of a liquation, from the beginning of putting in the charge till the last cake has been cast, depends of course on the size of the calcarone, and also on the nature of the stuff; a porous ore will work quicker than a compact ore, as the heat penetrates it more readily.

Atmospheric conditions have a certain influence on the duration of the liquation: wind increases the combustion and accelerates the production; rain, on the other hand, cools down the whole mass and retards it. On an average—

For a calcarone of 50 to 60 casse, the liquation lasts 30 to 35 days.

For a calcarone of 200 to 250 casse, the liquation lasts 50 to 60 days.

For a calcarone of 400 to 500 casse, the liquation lasts 80 to 90 days.

When the liquation is finished, the calcarone is allowed to cool gradually; if it were uncovered and allowed to cool rapidly, a large quantity of sulphurous acid would be evolved all at once, which would be injurious to crops or trees in the neighbourhood.

If the liquation proceeds properly, the first sulphur that runs out does not exceed in temperature 120° to 130° C.; but as the operation goes on, and the fire approaches the *morte*, the calcarone *runs hotter*, and the sulphur assumes that brown colour which is peculiar to it after it has passed through the viscous state. In some places the temperature must exceed 440° C., as little deposits of sublimed sulphur are formed on the outside covering towards the end of the operation. When a calcarone *runs too hot*, water is thrown in at the *morte*, which may cool down the sulphur there, and prevent its burning, but cannot have much influence on the general temperature of the heap.

With regard to the earthy ingredients of the ore, the limestone undergoes a superficial calcination, and the clayey parts get a reddish tint, which indicates an incipient baking. The ores with a gypseous gangue give the worst results, because gypsum at a temperature very near that at which sulphur fuses loses its water, and the loss of sulphur is increased by the amount that has to be burnt to evaporate this water.

Atmospheric agencies have a most sensible influence on the working of a calcarone. If the mineral was wet before it was charged, the loss of sulphur is of course increased by the extra quantity burned to dry the ore; if heavy rains come on, the water penetrating into the interior of the mass may so lower the temperature as to cause the operation to be a complete failure. The violence of the wind may accelerate the combustion too much; the calcarone heats, and there is loss of sulphur by volatilization, besides which the sulphur obtained when a calcarone runs too hot is always of inferior quality.

In a well-conducted calcarone, with an ore containing 25 per cent. of sulphur, 70 per cent. of marly limestone, and 5 per cent. of hygrometric water, the combustion of one-fifth of the sulphur would give heat enough theoretically to melt the remainder. In reality the loss of sulphur is one-third, or even two-fifths. The difference represents the loss by sublimation, by sulphur contained in the residues, by dispersion of heat, and by chemical reactions taking place during the operation.

At the sulphur mines it is usual to speak of the number of lumps, cakes, or ingots (*balate*) of sulphur produced per *cassa* of ore. Rich ore gives 12; medium, 8 to 10; poor, 6 ingots per cassa. This corresponds to a yield of 20, 15, or 10 per cent., or a real contents of 30, 23, or 15 per cent. The expression used at the sulphur mines is, however, very elastic, as the weight of the ingots and size of the *cassa* vary considerably. The cost of a calcarone of medium size—from 200 to 250 *casse*—is 6 to 7 francs per *cassa* of capacity; smaller ones cost more, larger less, per cassa. Calcaroni of 100 casse cost 8 francs per cassa capacity; those of 500 casse cost 5 to 6 francs per cassa.

The small ones are most convenient. From what has been said above, it is easy to come to the conclusion that the simplicity of the operation and the small cost of labour are the only advantages of the calcarone, which otherwise is a very imperfect apparatus, for the following reasons:—1. In the calcarone a considerable quantity of sulphur is burnt uselessly. 2. The apparatus cannot be properly attended to, and it is impossible to remedy properly any disturbances which may be observed in the course of the operation. 3. Large quantities of sulphurous acid are evolved, causing sensible damage to vegetation—so much so that where a calcarone is less than 200 yards from a house, or 100 yards from cultivated land, it can only be used from 1st August to 31st December. The consequence is that many mines have to liquate in four or five months all the ore extracted in the year. Some have not space to stock all their ore. The ore suffers from being exposed for so long a time to the weather, and much capital is locked up and rendered useless for two-thirds of the year.

Cost of the Sulphur.—The average cost of the ore may be taken as follows:—

	Francs per Ton.
Breaking,	1·70
Conveyance to the surface,	2·00
Oil and tools,	0·40
Stacking * and sundries,	0·20
Repairs of levels,	0·60
Pumping water,	0·20
	5·10

The average yield of the ore in the calcarone being about 14 per cent., 700 kilos. of ore are required to yield 100 kilos. of sulphur. Consequently we obtain—

	Francs.
700 kilos. of ore, at 5·10 francs per ton,	3·57
Cost of liquation,	0·53
General expenses of all kinds,	1·00
	5·10
Rent to the proprietor of the soil,	1·50
Total cost of 100 kilos. of sulphur at the mine,	6·60

* The ore is stacked when brought up from underground for the purpose of estimating its amount, the miners being paid according to the quantity excavated or amount of sulphur produced. This stacking has been very properly done away with at the Giona mines. The ore is trammed directly from the shaft to the *calcaroni*, and the quantity estimated at the rate of 12 trams. to a *cassa*.

The cost of 100 kilos. of sulphur, f.o.b., at ports in Sicily may be taken (1871) at—

	Francs.
Cost at the mine,	6·600
Carriage to the coast,	2·480
Shipping charges,	0·313
Profit of lessee of mine,	1·607
Export duty,	1·000
	12·000

When the railways and provincial roads are completed, as well as the harbours at Licata and Girgenti, there will be a considerable saving in the cost of carriage and shipping. It will then probably be possible to put the sulphur, f.o.b., at these ports for 10·50 francs the 100 kilos., or 105 francs per ton (1000 kilos. or 2240 lbs.).

Durand's Kiln. *—This is merely a modification of the ordinary calcarone. DURAND'S kiln is a rectangular chamber, 6 feet 6 inches square, with an inclined floor, and covered by a vaulted roof, which has a hole in the centre, through which the charge is introduced. On the sides are two doors for removing the charge. The sulphur runs out as in any ordinary calcarone, but the products of combustion are carried into a long flue, where some sublimed sulphur is deposited.

6. *Distillation in Iron Retorts.*—The plan used in the Romagna is as follows:†—The fireplace, *a*, and the flue, *b* (Figs. 9 and 10), are covered by a common arch, *c*, of fire-brick, which is provided with openings, *l*. The side wall of the hearth rises 3 feet 3 inches above the top of the arch, at an angle of 27°. Into the open space formed by the arch and the two side walls and end of the hearth eight retorts are placed, as shown in the figure. A second arch covers the whole, and only leaves the mouth of the retorts free.

These retorts are of cast iron, and made egg-shaped; close under the mouth is a little tubulure, *f*, or sometimes two such tubulures. This allows a retort to be turned round, if one side is very much worn. Iron pipes are cemented into these tubulures, and led into a condenser, *h*, common to two retorts. Under each condenser there is an iron basin, *i*, standing over a cavity, *g*, which communicates with the hearth and chimney by passages, *k*, *k*, *k*. By this means a current of hot air is made to pass under the basins, and keep the sulphur melted.

When the retorts have been filled with ore, the covers are put on and luted with clay. The flame draws into the flue, passes through the holes, *l*, and heats the retorts. The moisture in the ore is soon driven off, and the sulphur begins to escape as vapour. The vapour goes through *f* and *j*, and condenses in *h*; the molten sulphur then flows into the basin, *i*, when it is ladled out and poured into moulds.

The removal of the residues from the retorts is

* Parodi—*Op. Cit.*, p. 57 and Table II., Figs. 1, 2, 3, 4.

† The following account is taken from an article in the "Berg und Hüttenmännische Zeitung," vol. xxxiii., 1874, p. 343, which is itself translated from the "Bulletin de la Soc. de l'ind. minér." 1873, p. 609.

troublesome, as the workman has to stand in a very inconvenient position in order to reach down to the bottom of the retort with a shovel; whilst, at the same time, he is exposed to the sulphurous fumes which are still being given off. A complete operation lasts twelve hours, and each retort distils in twenty-four hours 300 kilos. (about 6 cwts.) of ore.

Fig. 9.

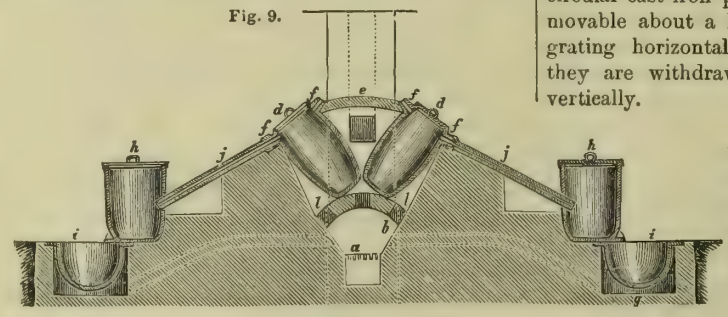
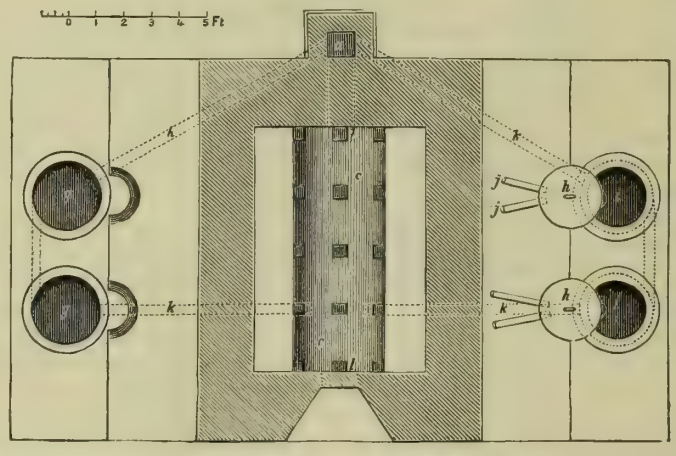


Fig. 10.



At Radoboi, in Croatia, the mineral is heated in a cast-iron pan, and the sulphur vapour at once conducted into a large chamber. The vapour condenses, and flowers of sulphur are deposited on the walls.

7. *Liquation by Means of Steam.*—The great loss of sulphur in the calcarone process has induced the trial of numerous other plans; and a company in Italy has introduced Thomas' apparatus, in which the melting of the sulphur is performed by steam, at a pressure of from 3 to 5 atmospheres.* Plate I. shows a modification of E. Thomas' apparatus, introduced by M. Pirckhey at the sulphur mines of Latera, in the province of Rome, where the ores contain 13 to 14 per cent. of sulphur.

The conical vessel, *a*, made of $\frac{1}{2}$-inch iron plates, is provided at both ends with cast-iron flanges, *b b'*, through which bolts pass for making the joints. The vessel is supported by means of flanges, *c c*, on iron beams, *d*, which are carried on iron columns, *f f*. Inside this vessel is a second cone, *g*, made of $\frac{3}{8}$-inch plate, and pierced with holes. It is fastened by bolts to the flange, *b'*. At the lower part of the vessel, *a*, there is a grating, *a'''*, formed of two semicircular cast-iron plates, perforated with holes, and movable about a hinge. Two screws, *h*, keep the grating horizontal during the filling; and when they are withdrawn, the two halves hang down vertically.

The inner cone, *g*, serves to receive the ore. The arrangement of the holes, their size, and the conical form of the apparatus are of the greatest importance, both for the liquation and subsequent removal of the residues.

The top of the vessel, *a'*, is closed by means of a cast-iron cover, *i*, and india-rubber washer; the iron ring, *j*, is used in moving it. To the under part of the vessel, *a''*, is fixed a cast-iron receiver, with a steam jacket. It can be moved away on a trolly, running on rails, when the operation is finished, so as to allow the residues to be emptied. This receiver is provided inside with a perforated plate of cast-iron, *n*. At its base is a pipe, *o*, with a specially-shaped iron tap for drawing off the condensed water and molten sulphur. The external vessel, *a*, is provided with two pipes:—One, *p*, carries the valve and steam pipe, besides a steam-gauge and pyrometer; the other, *q*, is the outlet of the steam.

The pipe and valve, *r*, connected with *r'* by a pipe with screw joints, leads the steam into the space, *l*, and keeps the receiver at the temperature of melting sulphur. The cocks, *s*, serve for cleaning. The outer vessel, the reservoir, and pipes are all surrounded with a bad conductor of heat, kept together by wooden staves. The tube and cock for the outlet are so arranged that the steam from an apparatus that has finished a charge can be drawn off and led into another. The exhaust steam is used for warming the feed water.

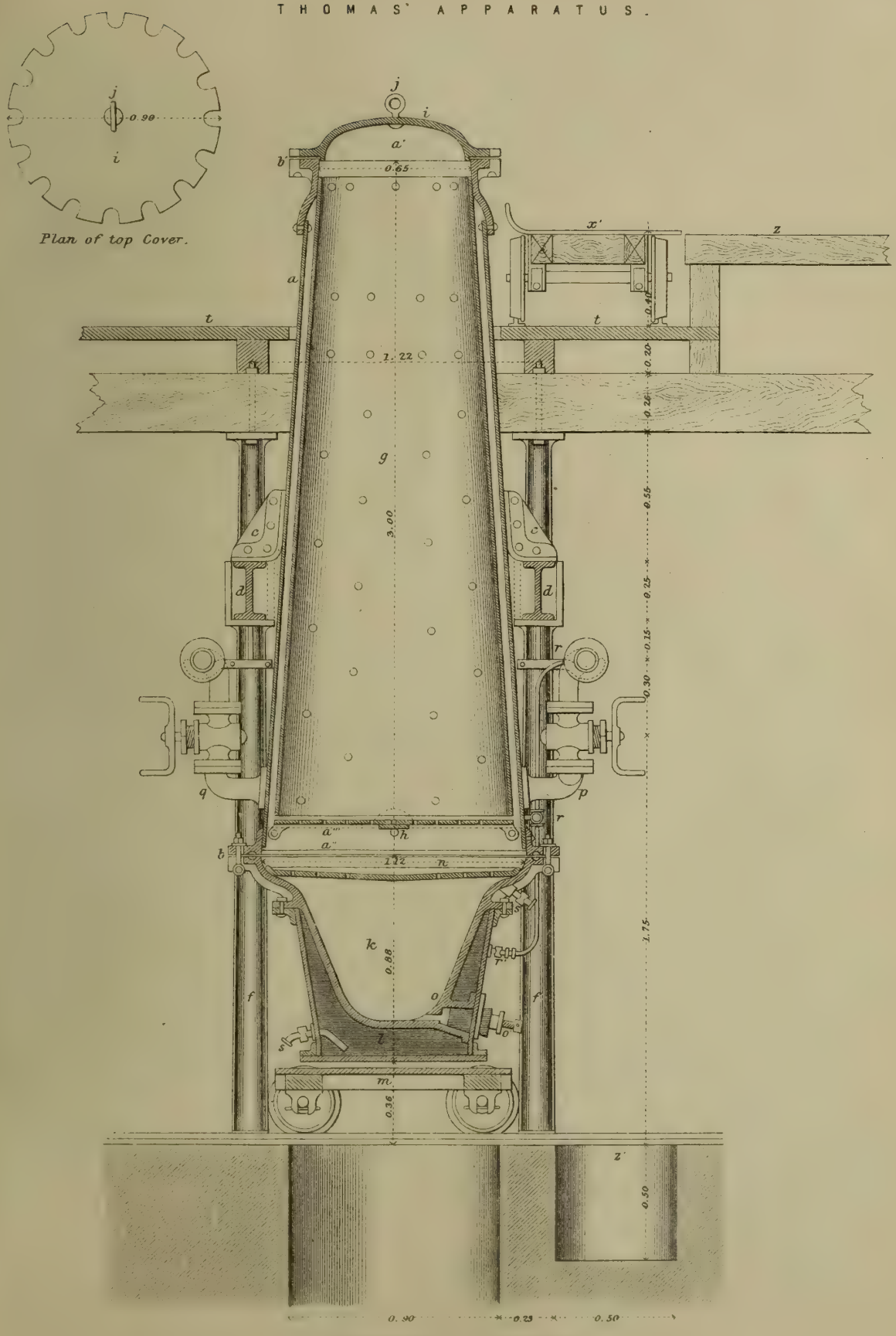
The pillars, *f*, prolonged above the beams, *d*, carry the beams which form the working floor, *t*. A tramway, *x*, with the trolly, *x'*, serves to connect all the apparatuses. The tram-waggons from the picking floors come in at the level, *z*, are carried by the trolly, and tipped into any apparatus. Under each apparatus there is a shaft, 26 feet deep; these shafts are connected with the mine by a level, and serve for carrying off the residues.

This arrangement may naturally be modified according to the position and requirements of the mine. The important point, however, is that this arrangement allows the residues to be removed very rapidly. Above the top of the apparatus, and on a frame not shown in the figure, there is a small carriage, with a differential pulley, which serves

* "Journal of the Society of Arts," 1st May, 1868.

SULPHUR.

THOMAS' APPARATUS.



J. B. LIPPINCOTT & CO. PHILADELPHIA.

for moving the grating, a''', and the cover, i. The six apparatuses at Latera are supplied by a cylindrical boiler, fired with wood, 4 feet 5 inches (1·35 metre) in diameter, and 43 feet 8 inches (13·30 metres) long.

From the above description the method of working is easily understood. The cover, i, is lifted off, the grating, a''', brought into a horizontal position, and three waggons of ore are tipped into the apparatus. The cover is then firmly bolted on. Whilst this is being done above, the receiver, k, is brought under the apparatus, the joint made tight, and the cocks, $r\,r'$, connected. Steam is now let in; it first of all condenses on meeting with the cold damp ore, and the temperature of the ore gradually rises till at last it reaches that of the steam (125° to 135° C., or 257° to 293° Fahr.); the condensed water is run out of the receiver, and soon the sulphur melts and runs out of the ore.

After a lapse of thirty to fifty minutes the ore is desulphurized, and the sulphur has collected in the receiver. The steam is now shut off, and turned on into an adjoining apparatus. On opening the cock, o', the sulphur runs out into a wooden mould standing in the pit, z', and the operation is finished. The connection with the adjoining apparatus is broken, and any steam remaining allowed to escape. The cover and the receiver are removed, and the screws, h, drawn back. The grating opens, and the desulphurized ore falls down into the shaft and is used in the mine for filling up the excavations.

The whole operation lasts from one and a half to two hours; it does not do, however, to reckon upon more than eight operations in the twenty-four hours. Each apparatus will take 53 cubic feet (1½ cubic metre) of ore. The temperature required varies with the ores, but 293 Fahr. (135° C.) is generally sufficient. The mine at Latera furnishes a very compact ore, which is not thoroughly acted on by this temperature. The average contents at Latera amount to about 13 per cent.; the yield is 11½ to 11¾, so that 1¼ to 1½ per cent. of sulphur remains in the residues. Each operation, with about 25 to 27½ cwts. (1300 to 1400 kilos.) of ore yields about 3¼ cwts. (165 kilos.) of sulphur, and requires as fuel 2½ cwts. (130 kilos.) of medium quality oak, with 10 per cent. of water. The amount of fuel will vary very little with the yield; it would be more, perhaps, in treating very compact ores.

In order to compare the steam and calcarone and doppione processes exactly, we assume that it is the case of a mine furnishing yearly 30,000 tons of ore with 20 per cent. real contents of sulphur, the cubic yard weighing 19½ cwts. (1 cubic metre weighing 1300 kilos.). In reality, it is only the steam apparatus and calcarone that come into competition, because the *doppioni* are only fit for a small output, require ore with very little or no moisture and much fuel, and are soon worn out as the iron gets eaten away.

A furnace with eight retorts, working 20 per cent. ore, yielding 17 per cent., can make two distillations in twenty-four hours, working over 2400 kilos. (47 cwts.) of ore, and producing 408 kilos. (8 cwts.) of sulphur. Omitting a sinking fund and general expenses, a ton of sulphur under these circumstances would cost:—

	Francs.
5,900 kilos. 20 per cent. ore, with 20 per cent. yield, at 4 francs 60 cents. * per ton,	27·14
2,500 kilos. wood, at 15 francs per ton,	37·50
Wages,	18·75
	83·39

This holds good for ores like those found at Latera. In the case of the more fusible ores in the Romagna three distillations may be made in the twenty-four hours, and the cost of fuel and wages becomes less, so that the cost price is reduced from 83 francs 39 cents. to 64 francs 63 cents.

A doppione furnace, with eight retorts and a shed, will cost from 3500 to 4000 francs.

Cost of 1 ton of sulphur by the calcarone process, excluding sinking fund and general expenses:—

	Francs.
7,140 kilos. 20 per cent. ore, yielding 14 per cent. at 4 francs 60 cents.,	32·84
Filling, liquation, &c.,	6·75
Superintendence, storing, &c.,	1·35
	40·94

Cost of 1 ton of sulphur, with the steam apparatus:—

	Francs.
5,405 kilos. of 20 per cent. ore, yielding 18½ per cent., at 4 francs 60 cents. per ton,	24·86
Filling, liquation, &c.,	5·65
360 kilos. oak, with 10 per cent. moisture, or 160 kilos. coal at 65 francs per ton,	10·40
Superintendence, storing, sundries,	2·50
	43·41

It has been assumed that the eight apparatuses will make 57 liquations in twenty-four hours, three charges being put through every eight hours. Each apparatus working through 1950 kilos. of ore as a charge would give 360 kilos. of sulphur; in twenty-four hours, therefore, 20,502 kilos. of sulphur would be obtained, and the assumed annual out-put of 30,000 tons would be worked through in 270 days.

Taking 100 francs as the value of the ton of sulphur at the mine, we get for the calcaroni—

	Francs.
4200 tons, at 100 francs,	420.000
Expenses, 4200 × 40·94,	171,948
Profit,	248,052

For the steam apparatuses—

	Francs.
5500 tons, at 100 francs,	550,000
Expenses, 5500 × 43·41,	238,755
Profit,	311,245

We have therefore a sum of 63,193 francs in favour of the steam process. However, the original cost and expense of repairs—*i.e.*, the sinking fund—alter this result considerably.

Working with calcaroni on the scale above mentioned would require at least 30 apparatuses, at

* This is 50 centimes less than the sum mentioned by Signor Parodi as the cost of the ton of ore on the mine.

1400 francs = 42,000 francs, which might be paid off in eight years, with a yearly sinking fund of 4398 francs.

The steam process in Sicily requires—

	Francs.
Eight apparatuses (40 tons each),	50 000
Two steam boilers and chimney,	28,000
Jacketing, pump, framework,	4,000
Masonry, roofing, &c.,	12,000
	94,000

These figures are estimated according to the prices of ironwork in Sicily in 1873, including carriage and duty.

The cost of the apparatuses should be paid off in five years, that of the boilers and sheds in ten years. This would require an annual sinking fund of 16,473 francs; therefore the above-mentioned profit of 63,193 francs would be reduced to 46,720 francs. The steam process therefore still effects a very considerable saving. The ores, too, can be worked over as fast as they are raised, and there is no necessity for storing the ore for a considerable time, as is customary in Sicily. Finally, the workmen can easily be paid according to the amount of sulphur produced. The process is carried on in inclosures, and there is no fear of any sulphur being stolen.

The mode of leasing mines in Sicily prevents many lessees from introducing these apparatuses. The mines are let out for a certain number of years on condition of giving up 20 to 35 per cent. of the produce in kind. Under these circumstances the steam process would be particularly advantageous to the proprietor or "lord" of the mine, but not so much so to the lessee.

If the rent were 30 per cent. of the out-put, the profit of the lessee would only be increased 13,448 francs, whilst the lessor or "lord" of the mine would get 1665 tons of sulphur instead of 1260 tons, and would thereby gain 40,500 francs.

We have not taken into consideration any royalty for the use of the patent. It may now be seen what an error inventors made who only looked at the higher yield, and not at the total cost of working, and asked for a royalty of 4000 to 5000 francs for each apparatus. With the expensive fuel in Sicily and the Romagna, the steam process will only be possible where the patent royalties are very small, as at Latera, or where the patent rights have lapsed.

The steam apparatus now used at Castel Termini differs from that of Pirckhey. It consists of a cylindrical vessel of cast iron, about 16 feet long by 4 feet in diameter, closed at one end. It is mounted like a gun on trunnions. The cylinder is charged with the open end uppermost, the cover is then fastened on, and the cylinder turned to a horizontal position; steam is let in, and the liquation of the sulphur effected. The sulphur is run off by tilting the cylinder, and finally, the spent residues are discharged by removing the cover. The horizontal position during fusion is found to be preferable, as the melted sulphur has only to drain through a height equal to the diameter; whilst, if it were maintained in a vertical position, it would have four times that distance to drain, and the time for a fusion would be considerably lengthened. There is a great loss of time in loading and unloading, and as compared with the *calcaroni*, a very small quantity of ore can be treated at one time. Admitting all the defects of the *calcaroni*, it is doubtful whether anything has yet been invented to supersede them entirely, for the cost of liquation is so small, only about 5 francs per *cassa* of 6·40 cubic metres (8⅓ cubic yards).

8. *Extraction of Sulphur by Bisulphide of Carbon.*—The process proposed by Bollmann consists of three operations:—1st. Desulphurization of the ore by means of successive washings with bisulphide of carbon in a series of vessels communicating with one another. The ore and the solvent should pass regularly from one vessel to another in the inverse sense; that is to say, the first vessel should contain nearly exhausted ore and pure bisulphide of carbon, and the last bisulphide of carbon all but saturated, and fresh ore. 2nd. Distillation of the saturated solution of sulphur in a retort heated gently. The sulphur is obtained as a residue, and the bisulphide of carbon condensed at the same time serves for another operation. 3rd. Separation of the bisulphide of carbon mechanically mixed with the sulphur by means of a jet of superheated steam. The bisulphide is condensed with the steam, and separates itself as a layer floating on the water. The process was tried in 1868, near Naples, but it has not been introduced at any sulphur mines; indeed, it is doubtful whether it could be worked profitably on a large scale. Pelouze * proposes to dissolve out the sulphur from poor ores and Laming's mixture by means of coal-tar oils.

Determination of Sulphur in Sulphurous Earths.—A rough and ready method of determining the quantity of native sulphur is to weigh out a quantity of the ore and set fire to it. The loss of weight by burning gives roughly the amount of sulphur. A more exact method is to use bisulphide of carbon to dissolve out the sulphur; in fact, the method proposed for extracting sulphur on a large scale. According to Anthon, † "2 grams. of coarsely pulverized ore are heated in a glass tube of 10 to 16 inches in length and 4 lines in width, which is closed on one side, and into the open end of which another tube, also closed on one side, is introduced up to within 3 inches of the ore. When no more sulphur issues from the ore, that piece of the latter tube in which the sulphur has been condensed is cut off and weighed. The sulphur is then removed, and the empty tube weighed again, the difference of the two weights giving the available amount of sulphur in the ore." For treating larger quantities an earthen retort is used, and the sulphur that distils over is collected and weighed.

Direct Extraction of Sulphur from Iron Pyrites and other Sulphides.—The immense quantity of sulphur stored up in the shape of

* *Berg und Hüttenmännische Zeitung*, vol. xxxi. p. 184, 1872.

† Statistics of Mines and Mining R. W. Raymond, Washington, 1873.

sulphate of lime and baryta, as well as the sulphides of iron, zinc, lead, and copper, is almost beyond calculation. There is good reason to suppose that at some future time little of the sulphur combined with these metals will be lost. The sulphur that is used in the manufacture of sulphuric acid is now mainly derived from the metallic sulphides, and the element itself can also be obtained from some of them. Iron pyrites, FeS_2, when heated in a close vessel, yields a part of its sulphur, some chemists say one-third, others three-sevenths. The reactions being $3FeS_2 = Fe_3S_4 + 2S$ and $7FeS_2 = FeS_2,6FeS + 6S$. Copper pyrites also evolves some of its sulphur under the influence of heat. Sulphur may be extracted from iron pyrites—1st, by roasting in heaps and kilns; 2nd, by distillation in closed vessels.

Roasting in Heaps and Kilns.—In roasting pyritous ores in heaps some sulphur is obtained by making little pits or holes in the top. The sulphur which is set free from the pyrites by the heat of the roasting condenses in the pits, and is ladled out from time to time. It is by this means that sulphur has been got from the Rammelsberg ores, treated at Oker in the Lower Hartz.

At Agordo, in Venetia,* a cupriferous pyrites is roasted either in heaps or kilns. Round holes are made in the upper surface of a heap about 11 inches in diameter by 4 inches deep, and the liquid sulphur is taken out by iron ladles. Obtained in this way the sulphur is very impure, being contaminated with arsenic, as well as with other metallic and earthy matters carried off during the distillation, or brought away mechanically during the ladling out. In order to purify it somewhat it is remelted, the floating scum skimmed off, and the sulphur poured into wooden moulds. This operation effects the separation of the earthy and some of the metallic matter, but not of the arsenic with which it is largely contaminated.

The Styrian kilns used at Agordo have a rectangular base about 56 feet long by 13 feet wide. The side walls are about 10 feet high, with two sets of openings left in them; the one to let in air to supply the combustion, and the other leading into little niches or chambers for collecting sulphur that is volatilized. Kilns have also been employed for roasting cupriferous pyrites of Wicklow, Fahlun, and Huelva,† and a small proportion of the sulphur obtained as a by-product.

Distillation of Pyrites in Retorts.‡—In the neighbourhood of Falkenau in Bohemia iron pyrites and marcasite, containing about 50 per cent. of sulphur, are distilled in fire-clay retorts, and about 20 per cent. of sulphur is obtained. The residues are piled up in heaps and exposed to the weather, and after the lapse of from one to three years the heaps are lixiviated, and green vitriol obtained.

* Statistica del Regno d'Italia, Industria mineralia, Relazione degl' Ingegneri del Real Corpo delle Miniere. Florence, 1868.

† *Berg und Hüttenmännische Zeitung.* vol. xxiv., 1865, p. 202.

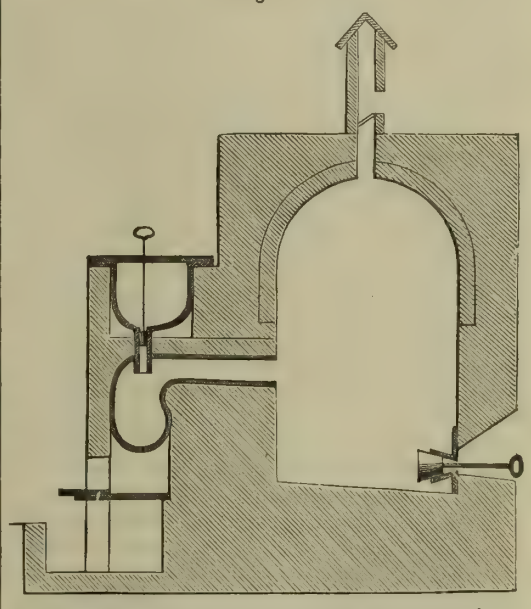
‡ *Denkbuch des Osterreichischen Berg und Hüttenwesens.* 1873, p. 140.

A similar process is used for distilling pyrites in Silesia.

Extraction of Sulphur from Alkali Waste.—See Soda, vol. ii. p. 843.

Refining of Crude Sulphur.—The sulphur obtained by liquation from the *calcaroni* is not sufficiently pure for all purposes, and has sometimes to be submitted to a process of refining. In 1815 a manufacturer named Michel, of Marseilles, devised an apparatus which, with some slight modification, is used up to the present day. The drawing (Fig. 11) represents a retort wherein the sulphur is converted into vapour, and a condensing chamber in which this is reconverted into solid sulphur. The apparatus, as in the drawing, consists, first, of a retort, C, beneath which is a furnace, A; this retort

Fig. 11.



is filled with liquid sulphur from the reservoir, B, wherein the crude sulphur is melted by the waste heat of the furnace to facilitate its introduction to the retorts. When the retort has become sufficiently hot, the sulphur begins to pass as vapour through the tube or opening, D, into the condensing chamber, E. This chamber is built entirely of brick, with a well-cemented brick floor. On its upper part a small chimney is erected; this chimney contains a sort of wooden valve or door, capable of opening outwards, to allow the expanded air to escape, and in case of explosion to allow the gases produced immediate exit. This apparatus when cold allows solid sulphur to form at once in the shape of the ordinary commercial *flowers* of sulphur; the vapours immediately on coming into contact with the cold chambers are chilled, and fall as a minutely divided solid. These flowers, as they are called, are removed before the chamber gets hot, which is the case after a few days' working, the whole of the heat which the sulphur had taken up, in order to become vapour, being given out to the walls; they thus acquire so

high a temperature as to fuse sulphur, therefore it can no longer become solid in contact with them, but condenses on their surface in a liquid form, and runs to the bottom, where it collects. When the operator is satisfied that sufficient has distilled over, he proceeds to remove it; this he does by means of the plug apparatus, figured at F, which is simply an iron plug with a tolerably long shank or handle, as is shown in the drawing. By pushing this plug inwards he opens the passage for the flow of the liquid sulphur, which runs into suitable moulds, to form the *stick* or *roll* sulphur of commerce. The residue is raked out of the retort, which is immediately charged again by removing the plug which closes the tube or passage between the vessel, B, and the retort.

A better apparatus is figured in Payen's *Précis de Chimie*, in which two retorts are attached to one condensing chamber; these retorts are cylindrical, and resemble to a certain extent ordinary gas retorts. A portion of the door which closes the outer end of the retort is movable, to enable the operator to rake out the debris after distillation; the other end of the retort rises like a swan's neck before opening into the condensing chamber. Over these openings or orifices within the chamber hangs a damper or register in such a manner that it can, from the outside, be placed over them, thus cutting off all communication between the retort and the chamber. A fusing vessel heated by the waste heat is attached, as in the drawing just given. This description of apparatus has the advantage that by its means the operations can be rendered continuous. For instance, let one retort be called A, the other B; suppose retort A charged at a certain hour, and retort B charged some two hours later, it is certain that, if charged with an equal weight of raw material, the retort A would be ready for recharging two hours before retort B. Supposing this to be the case, the damper or sliding plate is allowed to fall over the opening of retort B, thus closing the passage between it and the condenser, and preventing the rushing back of any sulphur vapour. The cover is removed from the front opening, the impure residue raked out, after which it is again closed; the entrance into the condensing chamber is again opened; a charge of sulphur is run in from the fusing vessel, and the distillation again commences. During the whole of these operations retort B has been uninterruptedly at work; but eventually the same operations have to be performed in connection with it as have been detailed with respect to retort A. Thus between the two a constant stream of sulphur vapour is being perpetually driven into the condensing chamber; the work going on almost without interruption, as the retorts never want charging simultaneously.

Sulphur thus produced is almost pure. It is true that the sublimed sulphur in powder—that is, the flowers of sulphur—contains a small quantity of sulphur dioxide, which, when the sulphur has to be applied to certain purposes, must be removed by washing with water. This, however, is the only body with which it is contaminated; the roll sulphur is free from sulphur dioxide.

Combinations of Sulphur.—Sulphur enters into many combinations, both simple and complex; it combines with hydrogen, and, with a few exceptions, with all the metals, with oxygen in several proportions, with carbon, phosphorus, chlorine, iodine, and bromine.

Sulphides.—Sulphide of hydrogen, sulphydric acid, or sulphuretted hydrogen, H_2S, is the transparent colourless gas, well-known for its nauseous odour, which is most offensive when in very small quantity. It exists in many mineral springs, such as Harrogate and others. It is a product of the decomposition of many organic bodies, and is evolved by putrid bodies, and is the cause of the smell of rotten eggs, the albumen of which, in undergoing decay, gives off its sulphur, or a part of it, as sulphide of hydrogen.

The density of sulphuretted hydrogen is 17, hydrogen being 1. It may be liquefied by pressure of 17 atmospheres, at 50° Fahr. (10° C.), and even solidified by a powerful refrigeration. It is a most poisonous gas; air containing one-tenth of a per cent. of this gas causes the death of some small animals. It acts as a powerful narcotic. It burns with a blue flame.

The gas is soluble in water, which, when cold, takes up about its own volume; this solution forms a useful laboratory reagent.

Sulphuretted hydrogen may be prepared by adding an acid to any soluble sulphide, such as those of the alkalies or the alkaline earths, or to an insoluble sulphide, such as sulphide of iron or sulphide of antimony. The most general method consists in adding dilute sulphuric acid to sulphide of iron.

The decomposition which produces this gas is very simple—

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Finely powdered antimony trisulphide yields sulphuretted hydrogen when acted on by boiling hydrochloric acid. The reaction is thus—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Persulphide of hydrogen (H_2S_2 or H_2S_3) is produced in the form of oily drops, when a solution of potassium pentasulphide is poured into dilute hydrochloric acid. It is very unstable; the greatest care and precaution cannot preserve it more than a few weeks, even though it be sealed hermetically in a glass tube. It simply forms a link in the chain of combinations that sulphur is capable of forming.

Metallic Sulphides.—In speaking of the natural compounds of sulphur many of these have been named, and attention need here only be called to the fact, that the artificial formation of the metallic sulphides is of constant occurrence in analysis. By the property of forming soluble or insoluble sulphides chemists are able to separate the metals into three classes. The following metals are thrown down as sulphides by sulphuretted hydrogen from an acid solution—gold, platinum, mercury, silver, lead,

bismuth, and copper, *black* precipitates; antimony, *orange;* arsenic, tin, and cadmium, *yellow*. The following metals, though not precipitated from their acidified solutions, are thrown down as sulphides when sulphuretted hydrogen is passed through their alkaline solutions—nickel, iron, cobalt, *yellow;* manganese, *flesh-coloured;* zinc, *white*. The sulphides of barium, strontium, calcium, lithium, sodium, and potassium, are soluble in water.

Compounds of Sulphur and Oxygen.—Sulphur forms two compounds with oxygen — sulphurous oxide, SO_2, and sulphuric oxide, SO_3. The latter will be treated in the article on Sulphuric Acid.

Sulphurous Oxide, Sulphur Dioxide, Sulphurous Anhydride, Sulphurous Acid, SO_2.—The irritating vapour or gas given off by burning sulphur. It is a transparent colourless gas, thirty-two times heavier than hydrogen; it is capable of assuming the liquid form, like carbonic anhydride, sulphuretted hydrogen, and sundry other gases, at an increased pressure with a very low temperature. Faraday liquefied it with a pressure of from three to five atmospheres. Its boiling point is —10° C. (14° Fahr.). The rapid evaporation of the liquid anhydride under an air-pump generates enough cold to freeze it. Solid sulphurous anhydride is heavier than the liquid, and melts at about —79° C. Sulphurous anhydride may be produced either by the oxidation of sulphur or the abstraction of oxygen from sulphuric acid.

When sulphur is made to burn in oxygen gas or common air sulphurous anhydride is obtained. If it is desired to pass a stream of the gas through any liquid intended to absorb it, the sulphur must be burnt in a close vessel or apparatus, which has a strong aspirator attached; the vessel containing the liquid to be treated being placed between the gas generator and the aspirator. The method generally adopted for procuring sulphurous oxide is that of depriving sulphuric acid of one equivalent of oxygen by any convenient reagent. A mixture of strong oil of vitriol and sulphur heated in a flask, which has a delivery tube attached, serves very well.

Sulphurous anhydride as nearly pure as possible, in fact, quite pure if made to traverse a little water to take up any sulphuric acid carried over, may be obtained by heating sulphuric acid with one-third its weight of copper turnings or clippings. The reaction is as follows—

$$2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2.$$

Mercury may be substituted for the copper, when a like reaction takes place. As water dissolves at the ordinary temperature thirty-three times its bulk of sulphurous anhydride, the gas cannot be collected over water. Its high specific gravity, more than double that of air, allows the method of displacement to be employed, and it may also be collected by means of the mercurial trough.

Sulphurous acid, H_2SO_3, has been obtained in crystals by cooling a saturated solution of the acid obtained by passing the anhydride into water. A hydrated sulphurous acid is also known. The acid is considered to exist in all solutions of sulphurous anhydride in water. The acid and the anhydride are powerful reducing agents. Acid solutions of the manganates and chromates are decolorized by them—in the latter case green chromous salts are formed. For analyzing the commercial sulphites, it is only necessary to weigh out a stated quantity of the sulphite or hyposulphite to be examined, dissolve it in water, make it acid with hydrochloric acid, and then to note the number of measures of a normal solution of potassium bichromate required to be added to convert the sulphurous into sulphuric acid, and data are obtained, from which the amount of sulphurous acid in the sample may be easily calculated. This reducing property of sulphurous acid has been turned to advantage by Bunsen in the indirect analysis of various bodies; for instance, in the valuation of manganese. He places the manganese in a flask, treats it with hydrochloric acid, and passes the evolved chlorine into a solution of potassium iodide, each atom of chlorine sets free an atom of iodine. When the operation is over, he disconnects the vessel containing this iodine, and adds from a burette a normal solution of sulphurous acid until the precipitated iodine has disappeared. Two equivalents of iodine convert an equivalent of sulphurous into sulphuric acid, as follows—

$$H_2SO_3 + H_2O + 2I = H_2SO_4 + 2HI.$$

Thus, tracing the reaction back, one equivalent of sulphurous acid represents an equivalent of binoxide of manganese. This principle is applied in a variety of ways. The deoxidising power of sulphurous acid is taken advantage of by the chemist in the estimation of arsenic. When arsenic exists as arsenic acid, it is very slowly thrown down by sulphuretted hydrogen, whereas arsenious acid is easily precipitated. Sulphurous acid possesses the power of abstracting oxygen from arsenic acid, and reducing it to arsenious acid, so that if a stream of sulphurous anhydride be passed through the arseniate to be analyzed, after making it acid with hydrochloric acid, it is converted into arsenious acid, which facilitates its precipitations when one comes to employ sulphuretted hydrogen.

Sulphurous anhydride passed through a dilute solution of ferric chloride quickly reduces it to the ferrous salt—

$$Fe_2Cl_6 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

Sulphurous acid reduces salts of gold, throwing down the gold in the metallic state. It is capable of taking up the second equivalent of oxygen from almost every metallic binoxide.

Sulphites.—Acid sodium sulphite was at one time an article of commerce under the half-fanciful and half-true appellation of *antichlore*. It is now almost superseded as such by sodium hyposulphite. The name *antichlore* is derived from the use to which it is applied, viz., to correct the evil effects of an overdose of chlorine. In the bleaching of paper pulp, if any excess of chlorine or hypochlorite has been used,

the sulphite, on being added, neutralizes it. If, for the sake of illustration, we imagine chlorine to have been used, then—

$$2Cl + NaHSO_3 + H_2O = NaHSO_4 + 2HCl.$$

This hydrochloric acid can be taken up by any alkali, or will itself decompose a fresh portion of the sulphite, driving off sulphurous acid.

Sulphites are used by some in the manufacture of beet sugar. PROUST recommended them and a sulphurous acid solution as being antiferments, and having also other advantages. The following method of procuring it in large quantities was proposed by CALVERT, in a lecture delivered before the Society of Arts. He constructs a sulphur oven, such as is used in the manufacture of sulphuric acid. Within this oven the sulphur is burned, producing sulphurous acid. An earthenware tube, immersed in water, leads from this burner or oven to a tall wooden column filled with pumice-stone, or other suitable porous body. A cistern of water is placed on the top of this column, to which cistern a tap or valve is attached, by means of which a shower of water can be sprinkled on the pumice-stone, keeping it in a moist or wet state. The mixture of gases issuing from the burner, consisting of sulphurous acid, atmospheric air, and residual nitrogen, pass along the conducting tube, enter the column near the bottom, and pass up its whole length, thus meeting with the descending water. The sulphurous acid is absorbed, and a constant stream of the solution issues into a cistern placed at the bottom for its reception, while the residual gases pass out into the atmosphere.

Some brewers employ a solution of sulphurous acid to rinse out beer barrels after washing, as it possesses the property of arresting the acetic fermentation.

Sulphurous acid, when present in a free state in small amounts, is easily detected by its suffocating odour. It does not, like sulphuric acid, give any reaction with a salt of barium, except when combined with a base. This is on account of the sulphite of barium—unlike the sulphate—being soluble in free acid. When sulphuric acid is added to a salt of barium, sulphate of barium is formed, and the acid corresponding to the barium salt is set free. But this acid can exert little or no action on the sulphate of barium. Now, on adding sulphurous acid to a salt of barium, the sulphite of barium would dissolve in the acid set free. But in the case of a salt being added, this does not occur. No acid is set free to exert a solvent action. For instance, if to a solution of chloride of barium is added a solution of sulphite of sodium, a white precipitate of sulphite of barium will be produced—

$$Na_2SO_3 + BaCl_2 = BaSO_3 + 2NaCl.$$

Supposing it to have been doubtful whether the salt employed was a sulphite or a sulphate, one can now determine the point by the addition of an acid, say hydrochloric acid. Sulphite of barium being soluble in this acid, the precipitate will disappear if the salt was a sulphite; if the precipitate is persistent, a sulphate is indicated. Of course, both may be present.

An old specimen of sulphite is sure to contain a quantity of sulphate, formed by oxidation, even though pure originally. To determine absolutely the presence or absence of sulphurous acid in a body, it is only necessary to dissolve it in hydrochloric acid, if solid; or if a liquid, make it acid to the same extent, and add a few scraps of zinc. If the body under examination contain sulphurous acid, the hydrogen going off will be accompanied by sulphuretted hydrogen, which may be detected by the smell, or by its blackening paper dipped in a solution of a lead salt. This test will discover very minute quantities of sulphurous acid. Such is its delicacy that sulphurous acid may be detected in much of the commercial hydrochloric acid; it arises from the action of the strong sulphuric acid on the iron-decomposing vessel employed. The reaction may be explained as follows—

$$H_2SO_3 + 3Zn + 6HCl = 3ZnCl_2 + 3H_2O + H_2S.$$

One method of estimating sulphurous acid has been given; but the ordinary method is to convert it into sulphuric acid, and then proceed in the manner followed in the estimation of that acid. This may be effected by several oxidising bodies. It is sometimes recommended to employ nitric acid, but there is a chance of error by doing so, inasmuch as a quantity of the sulphurous acid may escape whilst heating it. Perhaps the best method is to pass through the sulphurous acid or the sulphite to be analyzed a current of chlorine until the liquid smells of the latter gas, placing it on a sand bath until all smell has disappeared, then precipitate with a salt of barium, collect, wash, ignite, &c., exactly as indicated under the head SULPHURIC ACID.

The conversion of a sulphite into a sulphate may also be effected by the dry way, by heating the salt in a platinum crucible with 4 parts of a mixture of equal parts of sodium carbonate and potassium nitrate (FRESENIUS).

Corresponding to sulphurous acid is a series of salts called sulphites, one of which has been already mentioned, the sulphite of sodium. These sulphites have been shown by Dr. MUSPRATT to bear a strong resemblance to carbonates, being also isomorphous with the latter salts. The following list proves the analogy:—

Sulphites.	Carbonates.
$K_2SO_3 + 2H_2O$	$K_2CO_3 + 2H_2O$
$KHSO_3$	$KHCO_3$
$Na_2SO_3 + 10H_2O$	$Na_2CO_3 + 10H_2O$
$NaHSO_3$	$NaHCO_3$
$NaHSO_3 + 4H_2O$	$NaHCO_3 + 4H_2O$
$BaSO_3$	$BaCO_3$
$SrSO_3$	$SrCO_3$
$MgSO_3 + 3H_2O$	$MgCO_3 + 3H_2O$
$MnSO_3 + 2H_2O$	$MnCO_3 + 2H_2O$
$PbSO_3$	$PbCO_3$
Ag_2SO_3	Ag_2CO_3.

Sulphite of sodium is the only salt—with the exception of a mixed sulphite of calcium and magnesium—which is manufactured on a large scale.

Sulphite of sodium is made by passing a stream of sulphurous anhydride through a solution of carbonate of sodium; carbonic anhydride is displaced, and sulphite of sodium is formed.

On the large scale, the same method as is pursued in the manufacture of bicarbonate may be followed for the production of the sulphite. A chamber or suitable large vessel is so constructed that a stream of sulphurous anhydride from burning sulphur may be drawn through. This chamber or vessel is filled with crystals of carbonate of sodium; the stream of sulphurous anhydride in its passage through the interstices of the mass is taken up, carbonic anhydride being evolved. The passage of the gas must be continued until a sample taken out of the chamber, on being dissolved, has an acid reaction with litmus paper. The mass of what was originally carbonate of sodium has now become a mixture of sulphite and bisulphite of sodium. This is now dissolved in water, and brought to the boiling point; a solution of carbonate of sodium must now be added, until the last addition causes no evolution of carbonic anhydride; the whole is now brought to the state of neutral sulphite; and after standing to deposit any mechanical impurities, may be run off into a suitable vessel to crystallize.

The sulphites of potassium and ammonium may be prepared in a similar manner to that of sodium, by passing sulphurous anhydride through a solution of the alkalies or their carbonates.

The sulphites of the metals of the alkaline earths are prepared either by exposing the moistened, or better, the hydrated oxides, to gaseous sulphurous anhydride, when this gas is absorbed; or the oxides or carbonates may be suspended in water, and a stream of sulphurous anhydride passed through, or they may be produced by double decomposition from a soluble alkaline sulphite, and a chloride of the earthy metal. These sulphites are all nearly insoluble in water and alcohol, but are rendered somewhat soluble by an excess of sulphurous acid, in this respect resembling the carbonates. The only practical purpose to which any of these earthy sulphites have been applied is as disinfectants. For this purpose a mixture of the sulphites of calcium and magnesium is used. Mr. M'DOUGALL seems to have a method of producing sulphites much more readily than any other maker.

The sulphites of the metals proper, such as iron, zinc, lead, bismuth, &c., are produced by analogous processes; they, like the earthy sulphites, are more soluble in a solution of sulphurous acid than in pure water.

Hyposulphurous, Pentathionic, Tetrathionic, Trithionic, and Hyposulphuric Acids.—In addition to sulphurous and sulphuric acids there are other acids of sulphur, in fact, the whole series is shown thus:—

Thiosulphuric or hyposulphurous acid,	$H_2S_2O_3$
Pentathionic acid,	$H_2S_5O_6$
Tetrathionic acid,	$H_2S_4O_6$
Trithionic acid,	$H_2S_3O_6$
Sulphurous acid,	H_2SO_3
Dithionic or hyposulphuric acid,	$H_2S_2O_6$
Sulphuric acid,	H_2SO_4

Thiosulphuric acid can scarcely be said to be known in the free state; when set free it splits up gradually into sulphur and sulphurous acid. The sodium salt, $Na_2S_2O_3 + 5H_2O$, commonly called hyposulphite of soda, is of considerable commercial importance. It is used as an antichlore for finishing bleached goods; and by photographers to dissolve unreduced silver salts. It may be prepared in various ways:—

1. By boiling the sulphite with sulphur. The reaction is most simple—

$$Na_2SO_3 + S = Na_2S_2O_3.$$

2. By heating carbonate of sodium with sulphur. Small quantities may be prepared thus:—1 lb. of pure crystallized carbonate of sodium is dried as perfectly as possible. When powdered, this is mixed with 5 ozs. of pure sulphur, the mixture heated in a glass or porcelain basin to the melting point of sulphur, and kept at that temperature for some time, stirring constantly in order to bring every part into contact with the air. The sulphide of sodium formed at first absorbs oxygen from the air, and is converted with feeble incandescence into sodium thiosulphate. The mass, when cold, is dissolved in water, and boiled with sulphur for some time, and the liquid evaporated to the crystallizing point. Very fine and pure crystals are obtained in this manner. If the heat be too strong, part of the sulphur is burned off, and carbonate of sodium remains undecomposed. In this case a second crystallization is requisite.

3. By passing a current of sulphurous anhydride through a solution of sulphide of sodium, boiling, filtering, and evaporating to the crystallizing point.

4. The earthy thiosulphates are formed by exposing their sulphides to the air; and this fact forms the basis of LOSH'S patent for the manufacture of hyposulphite of soda. LOSH exposes alkali waste to the atmosphere, lixiviates the weathered mass, dissolving out calcic thiosulphate. To this is added sodium carbonate, and by double decompositions calcium carbonate and sodium thiosulphate are the results. The latter crystallizes on evaporating the solution.

5. According to E. KOPP'S method, carried out industrially by MAX SCHAFFNER at Aussig, hyposulphite of lime is first prepared by causing sulphurous acid to act upon calcium sulphide (soda waste). The lixiviated mass is treated with sulphate of soda, the result being the formation of soluble hyposulphite of soda, and practically insoluble sulphate of lime. Very recently the pentathionic acid ($H_2S_5O_6$) obtained as a by-product of the reaction between sulphuretted hydrogen and sulphurous acid in separating sulphur, has been converted into hyposulphite of soda by boiling with soda lye—

$$2H_2S_5O_6 + 3H_2O = 5H_2S_2O_3.$$

Sodium thiosulphate is used to a small extent in analysis as a reducing agent; also as a means of separating iron and aluminium, dependent on the fact that aluminium thiosulphate is not stable at

much above the ordinary temperature. For instance, suppose iron and aluminium are both contained in a solution; to this solution is added as much sodium thiosulphate as will convert these bases into thiosulphates; this is done while cold. The solution is now heated to boiling. Aluminium thiosulphate decomposes at this temperature into sulphur, sulphurous acid, and alumina, while the iron being more stable remains intact. The whole is now thrown on to a filter, when the iron salt passes through, while the alumina remains on the filter; it is then washed, dried, and ignited. The iron is separated from the filtrate in the usual manner.

This reaction is used, though to a very small extent, in calico printing. Aluminium thiosulphate is formed in the cold by adding a solution of chloride of aluminium to a solution of hyposulphite of soda. The result is a solution of chloride of sodium and thiosulphate of aluminium. This is thickened in the regular manner, and printed on the fabric. The piece is then exposed to a temperature of 212° Fahr. by means of steam, when the salt is decomposed, alumina being deposited on or in the cloth. This alumina so deposited dyes up with madder precisely like the alumina precipitated in the ordinary manner from the acetate.

The value of hyposulphate of soda in photography consists in its power of dissolving the chloride, bromide, and iodide of silver. The photographic paper or plate, after exposure in the camera or printing frame, is "fixed" by a solution of sodium thiosulphate, which dissolves all the silver salt that has not been acted on by light. This property has been turned to practical account in metallurgy by Dr. Percy, followed by the Austrian chemist Patera. At Joachimsthal, in Bohemia, the silver ores, which contain also copper, lead, iron, zinc, nickel, cobalt, and bismuth, were roasted with salt, and the chloride of silver was dissolved out by hyposulphite of soda and then precipitated by sulphide of sodium. Calcium thiosulphate has been employed for a similar purpose, and also as an antichlore.

The other acids and their corresponding salts are of no practical importance, though of interest in a scientific point of view.

Sulphur and Carbon.—Sulphur forms several combinations with carbon; the one most marked and of the greatest importance, inasmuch as it is used in the arts, is the bisulphide of carbon or carbon disulphide—CS_2. It is formed by passing the vapour of sulphur over or through red-hot charcoal. This is effected by filling an iron or porcelain tube placed across a furnace with fragments of charcoal. One end of this tube is connected with a condensing apparatus plentifully supplied with cold water. The other end of this tube must be capable of being closed tightly with a cork. When the tube is sufficiently hot the cork is removed, and small pieces of sulphur are pushed through near to the charcoal. The orifice being again closed, the sulphur is converted into vapour, and in passing through the *interstices* of the *incandescent* carbon, combines with a portion of it, forming bisulphide of carbon, which, passing on to the condensing apparatus, collects as a liquid. After sufficient time has elapsed a fresh portion of sulphur must be introduced, the operation being continued in this manner until sufficient has been prepared. This product is by no means pure, containing more or less sulphur which has escaped combination, and from which it must be freed by distillation in a glass retort placed in a water bath.

In preparing bisulphide of carbon on a large scale the apparatus employed is a modification of that described above. A clay retort fixed vertically is filled with pieces of coke, and sulphur is introduced from the top by a porcelain tube which passes down nearly to the bottom of the retort; the sulphur vapour that forms is then obliged to traverse the incandescent coke, becomes converted into bisulphide of carbon, escapes by a tube at the top, and is condensed. (The apparatus is figured in Wagner's "Chemical Technology," translated by Crookes.)

Bisulphide of carbon has a density of 1·272. It is, as obtained above, a transparent, colourless liquid, of a strong disagreeable odour. This odour is due to a foreign body, the true smell being of a vinous or ethereal character. A considerable portion of this smell may be removed by shaking it up in a bottle with a quantity of strong sulphuric acid and bichromate of potassium. Bisulphide of carbon is very volatile, its boiling point being 43° C. It rapidly evaporates, almost equalling sulphuric ether in this respect, diffusing its odour through the apartment. It is a very effective solvent of fatty matter. Grease stains may be removed by it from paper or woven fabrics. The extraction of fat and oils from various substances by means of bisulphide of carbon is performed commercially on a large scale.

Among other substances soluble in bisulphide of carbon are phosphorus, sulphur, camphor, iodine, and india-rubber. As has already been stated, a process for the extraction of sulphur from some of its ores is founded upon the high dissolving power of the bisulphide, which will take up, if warm, about 60 per cent. of sulphur, and cold, from 25 to 30 per cent. Mixed with a little chloride of sulphur, bisulphide of carbon is used for sulphurizing, or, as it is commonly called, *vulcanizing* india-rubber. The addition of a few drops of bisulphide of carbon to a silver bath is found to facilitate the production of a bright deposit in electro-plating.

Sulphur and Chlorine.—There are three chlorides of sulphur—monochloride, SCl or S_2Cl_2; dichloride, SCl_2; and tetrachloride, SCl_4. The monochloride is used in the manufacture of india-rubber. It is prepared by passing chlorine gas through melted sulphur. The deep orange-coloured liquid that distils over is found to contain sulphur in solution. From this it must be freed by distillation, at a low temperature, and if necessary, the rectification repeated until its boiling point is stationary at 136° C., Fownes; 139° C., Odling; 144° C., Wagner. This chloride of sulphur has some curious properties; by means of it a species of artificial india-rubber may be produced. To procure this body take a quantity of

vegetable oil, say linseed or rape, and mix it with one-tenth its bulk of chloride of sulphur, and slightly warm the mixture; a strong reaction takes place, hydrochloric acid is disengaged, and a mass remains which, when washed with water, becomes white, and is as elastic as genuine caoutchouc, with precisely the same appearance. This curious body resists the action of boiling alkalies; ammonia and concentrated acids are without action on it, and it resists the solvent powers of alcohol, ether, bisulphide of carbon, and oils.

The dichloride is produced by passing chlorine into the monochloride whilst cooled by a freezing mixture of ice and salt. If the temperature be reduced to —20° C. still more chlorine is absorbed, and the tetrachloride is formed.

Iodide of Sulphur, SI_2, is used in medicine.

SULPHURIC ACID.— *Vitriolic Acid— Oil of Vitriol. Acide Sulphurique* (French); *Schwefelzäure* (German), H_2SO_4. A colourless, transparent, oily liquid, of specific gravity, 1·848: it freezes at — 26° C. (— 15° Fahr.), boils at 327° C. (620° Fahr.), and when heated passes off in colourless vapours, which produce a thick white cloud in contact with the mixture in the air. It is inodorous, and at ordinary temperatures it does not fume. It corrodes organic matters very strongly, and is coloured brown by them.

Geber, an Arab of the eighth century, obtained sulphuric acid by distilling alum; and Basil Valentine of Erfurt (born 1394) is the first to mention its properties as extracted from green vitriol (sulphate of iron). It was known also to Paracelsus, a Swedish chemist, who died in 1541. Gerard Dormeat gives an account of it in 1570. The formation of anhydrous sulphuric acid (sulphuric anhydride (SO_3)) by the burning of sulphur was first brought into notice in England in 1720. The composition of the anhydrous acid was examined by Richter, Klaproth, Bucholz, and Berzelius, and again very carefully by Stahl, and by Scheele in 1771; by Priestley in 1774, who first collected it as a gas over mercury; in 1782 by Bertholet; and in 1797 by Fourcroy.

Sulphuric acid exists in volcanic springs. It is found in large quantities in a torrent flowing from the volcano of Parcé in the Andes, and Boussingault has calculated that this stream carried down 15,000 tons of sulphuric acid yearly, and 11,000 tons of muriatic acid. A stream from an active volcano in New Granada has been found by Dagaulhardt to contain even greater quantities of sulphuric acid. Roberts has found sulphuric acid in the hot springs of the Solfatara Krisovik in Iceland. Free sulphuric acid (produced by the decomposition of iron pyrites) has occasionally been found in the coal mines of Northumberland. It exists in both the organic and inorganic kingdoms in combination with ammonium, potassium, sodium, barium, strontium, calcium, magnesium, aluminium, zinc, lead, copper, iron, &c.

Anhydrous Sulphuric Acid (*Sulphuric oxide or anhydride*, SO_3,) can be produced by heating fuming oil of vitriol in a retort, the neck of which passes air-tight into a perfectly dry receiver surrounded by ice: the sulphuric oxide distils over first, and then hydrated sulphuric acid. Sulphuric anhydride forms thin needle-shaped crystals, arranged in feathery groups, and of a white, opaque, asbestos-like mass. It is tough, and difficult to cut. Specific gravity, 1·954, and, in a liquid state, 1·97. It fuses at about 18° C., and boils at 35° C. when recently prepared; but subsequently assumes an allotropic condition, in which it remains solid up to 100° C., when it melts to a colourless liquid, whilst being heated to this temperature it volatilizes, and returns to its normal condition.

Sulphuric anhydride may be held for a time between the dry fingers, but soon produces a penetrating sensation. It hisses violently when thrown into water, forming sulphuric acid with evolution of heat. It produces dense white fumes in the air. It is very corrosive and poisonous. Its solution in water has a strongly acid taste, and reddens litmus paper, whereas the anhydrous sulphuric acid does not redden dry litmus paper. When sulphuric oxide (SO_3) is passed through a red-hot porcelain tube, it is resolved into a mixture of 2 volumes of sulphurous oxide (SO_2) and 1 volume of oxygen (Berzelius). Phosphorus takes fire in the vapour of anhydrous sulphuric acid at ordinary temperatures, and deposits sulphur in the form of a thick crust (Vogel). At ordinary temperatures the vapour of sulphuric anhydride does not act upon zinc, tin, lead, iron, copper, mercury, or silver.

F. C. Vogel has discovered that sulphuric oxide combines with sulphur in several proportions, forming a brown, green, and a blue compound, the first containing the most and the last the smallest quantity of sulphur. Wach prepared these substances by placing washed and well-dried flowers of sulphur and anhydrous sulphuric acid in alternate layers in a bent tube, which was sealed, and leaving them to act upon each other at a temperature between 16° and 19° C. The sulphur was first converted, with slight rise of temperature and evolution of gas, into a thick red-brown liquid, which, by taking up more acid, assumed a brown, green, or blue colour. Similar colours can be observed frequently in the strong "drops" of the ordinary sulphuric acid chamber.

Sulphuric acid (H_2SO_4) is intensely acrid and caustic; it acts rapidly upon the cuticle, occasioning a biting sensation and a soapy feel of the part, even when diluted. It is extremely sour, and it powerfully reddens litmus. It has a strong attraction for water, and in moist weather, if exposed, 3 parts increase to 4 in twenty-four hours. This property makes it useful in drying gases and other substances.

When sulphuric acid is suddenly mixed with water much heat is evolved, it can even be made to boil; 4 parts of acid, specific gravity 1·8, and 1 of water at 32° Fahr. (0° C.) produce, when mixed, a temperature of 212° Fahr. (100° C.) The greatest heat is evolved by mixing 73 parts of acid with 27 parts of water (Ure). Even a boiling temperature does not prevent sulphuric acid from taking up

moisture from the air, on which account it is necessary to use glass retorts or platinum stills in the place of open pans, to bring the acid to its highest strength. Four parts of acid and 1 of ice produce heat, but 4 parts of snow and 1 of acid produce cold (Brande).

Oil of Vitriol from Copperas. — Ordinary strong sulphuric acid of about 150° Tw. (specific gravity 1·750), easily freezes when standing in a carboy at about 40° Fahr. or under, and is difficult to liquefy again.

Sulphuric acid displaces the greater part of the other acids from their combinations, and at ordinary temperatures decomposes phosphates and borates; but at a red heat the phosphoric and boracic acids expel sulphuric and its bases. In consequence of its strong affinity for water it chars most organic matters, and it acquires a brown tinge from the smallest particles of straw or dust, &c. It dissolves small quantities of charcoal, as well as sulphur, tellurium, and selenium; and these bodies give it various shades of brown, red, and green, or blue. In consequence of its extensive use in manufactures, it is important to the consumer to have a ready method of ascertaining its strength. Several valuable tables have been drawn up by Dalhou, Parkes, and Dr. Ure, to show its strength and commercial value; the table by Dr. Ure is generally referred to as the standard. Glass hydrometers are used in large works to ascertain its strength, and are sufficiently trustworthy for general purposes. In taking the specific gravity of sulphuric acid it is very important to take the temperature into account, as it greatly influences the density. On removing a thermometer from the acid it rises to 75° or 80° Fahr.; by absorption of water it afterwards slowly falls to the temperature of the air. Again, if the thermometer has its bulb covered with a film of water, and be plunged into a strong acid, it will rise 10° Fahr. more beyond the real temperature. An elevation equal to 10° Fahr. diminishes the density of oil of vitriol by 0·005: 1000 parts being heated from 60° to 212° Fahr. becomes 1043 parts in volume, and the specific gravity, which was 1·848, falls to 1·772, being equal to a dilution of 14 per cent. of water.

Nordhausen Sulphuric Acid.—Fuming Acid. ($H_2S_2O_4$?) A thick oily liquid, generally of a brown colour. It is produced from dry ferrous sulphate, which is placed in a glazed earthenware or sometimes a green glass retort, which is exposed to a nearly white heat. The distillate (sulphuric oxide) is received in a small quantity of water, or better, in oil of vitriol, and forms a dark-coloured liquid of a specific gravity of about 1·9. It boils at 120° to 130° Fahr. When cooled, it deposits crystals of a compound of H_2SO_4 with SO_3. It smokes when exposed to the air, from the escape of volatile sulphuric anhydride. When heated it gives off sulphurous oxide, and sulphuric oxide remains.

Fuming sulphuric acid is now chiefly manufactured in Bohemia, and is in great request as a solvent for indigo; it is also largely used in the manufacture of alizarine. When the brown acid is kept at a temperature of 32° Fahr. it readily forms crystals, which are a definite compound of 2 atoms of anhydrous sulphuric acid, and 1 atom of water. The sulphuric anhydride may be separated from the brown acid, by careful distillation in a retort, into a dry and cold receiver. It passes over in drops, which concrete on cooling into a tenacious mass of crystals.

By careful management the calcined sulphate produces sometimes up to 30 or 40 per cent. of acid.

It may be safely stated that up to 1730 all sulphuric acid produced for commerce in England, was made from copperas (ferrous sulphate). The consumption was small, and the price was about two shillings per lb., or £220 per ton. The present price for similar acid is £4 10*s.* per ton.

Sulphur. — The next mode of making sulphuric acid was by the oxidation of sulphurous acid (produced by burning sulphur) in presence of vapour of water. This was the suggestion of two French chemists, Lefevre and Lemery, who added nitrate of potash to the sulphur in burning it; and the process was adopted in England by Dr. Ward about 1736, as follows:—The sulphur and nitrate of potash were suspended on an iron tray in a large wide-mouthed glass globe, partly filled with water; the mixture was set fire to by a red-hot iron, and then the mouth of the globe was closed. As soon as the charge was burnt another was inserted and fired, and this was repeated till the acid was found to be sufficiently strong, when it was removed into a glass retort and was concentrated. This acid, which was termed "oil of vitriol from the bell," sold for two shillings per lb., and was in much demand on account of its purity. In 1746 Dr. Roebuck of Birmingham put up the first leaden chamber in England, which was employed as a substitute for glass globes. It was small in dimensions, being about 6 feet square, and the charges of sulphur and nitre were burned in the chambers, much in the same way as in the glass globes. The success of this mode of making acid was so great, that others were erected at Preston Pans in Scotland, in 1749, by Roebuck and Garbett. Acid works were erected in London by Kingscate and Walker in 1772, and at Eccles near Manchester in 1783. (R. C. Clapham).

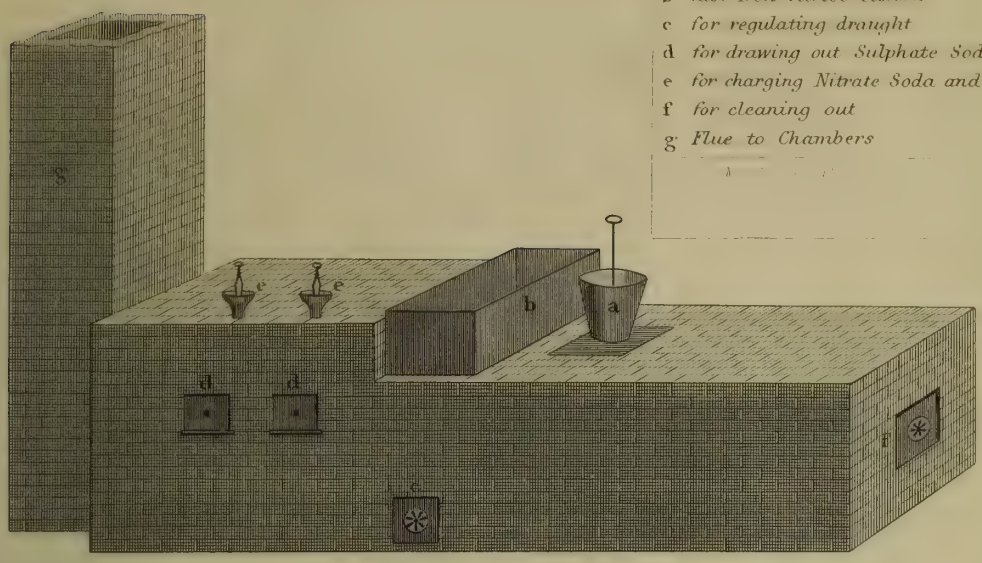
In 1797 there were in Glasgow alone six or eight acid works, and the following is a note of the cost of manufacturing 950 bottles:—

25 tons of sulphur at £40,		£1000	0	0
7 tons of nitre at £100,		700	0	0
Coals,		105	0	0
Wages and houses for workmen,		250	0	0
Tear and wear,		30	0	0
Rent and buildings,		70	0	0
Cartage,		40	0	0
		2195	0	0
142,500 lbs. of oil of vitriol at 6½*d.*	£3859 17 6			
Less 10 per cent. discount,	385 19 9			
		3473	17	9
Say the cost was £32 per ton, and the selling price was £54 per ton nett,	Profit	1278	17	9

(J. MacTear).

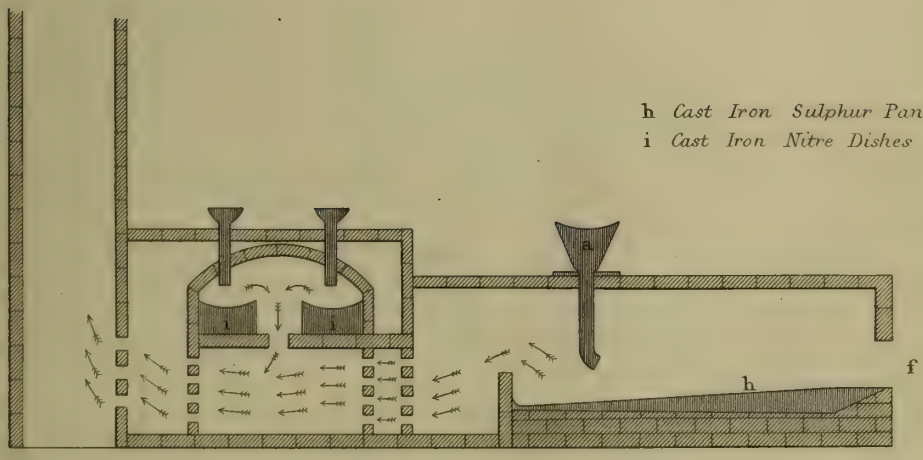
PYRITES KILN.

a *Funnel for feeding furnace*
b *Cast Iron Vitriol Cistern*
c *for regulating draught*
d *for drawing out Sulphate Soda*
e *for charging Nitrate Soda and Vitriol*
f *for cleaning out*
g *Flue to Chambers*

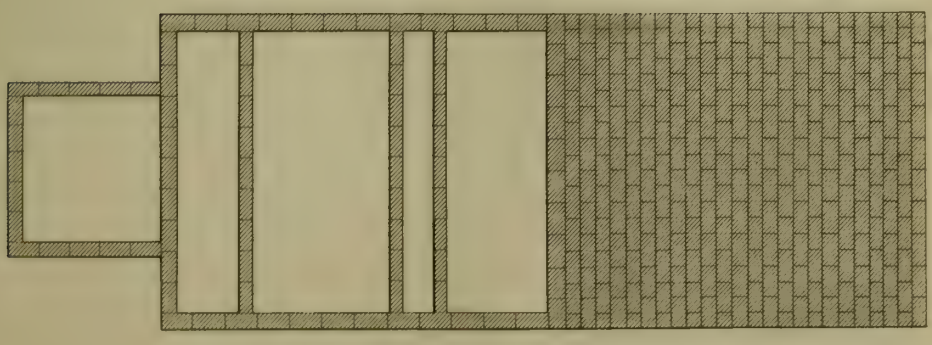


ELEVATION

h *Cast Iron Sulphur Pan*
i *Cast Iron Nitre Dishes*



SEGMENT



GROUND PLAN

J. B. LIPPINCOTT & CO. PHILADELPHIA.

Bealy and Radcliffe had works in Manchester in 1799: there were six chambers, 12 feet × 10 feet × 10 feet. Each chamber had a valve which was opened to allow the escape of the waste gases between the burnings. In these chambers 1386 lbs. of sulphur and 198 lbs. of nitre were burned weekly on iron plates or trays, of which there were two sets in each chamber, one placed over the other about $3\frac{1}{2}$ inches apart. The produce of oil of vitriol, of specific gravity 1·800, was 1800 lbs., equal to 130 per cent. on the sulphur and 14·3 per cent. on the nitre. The charge was burned off in about an hour, and then a new one was introduced every four hours. The strength of the acid in six days' working was 50° Tw. or specific gravity 1·250, and it was then run off and concentrated. The cost of this acid was £21 10*s.* per ton. and the selling price about £60 per ton. (J. MacTear).

Sulphuric acid chambers were erected at St. Rollox, Glasgow, in 1803; the sizes being 12 feet × 10 feet × 10 feet, and the sulphur burned in them weekly was about 10 cwts. and the nitre equal to 14 per cent. The residues or sulphur ashes in most works at that time, from a single burning, which was the usual practice, contained from 25 to 30 per cent. of sulphur left as waste, and it became a serious question what to do with them. C. Tennant & Co. of Glasgow were the first to begin to use them over again, and they purchased the ashes from other makers at £5 per ton. (J. MacTear).

The manufacture of oil of vitriol by the new method of acid chambers gradually superseded the old one from copperas, and the total produce of lead chamber acid so far increased, that in 1790 England became for the first time an exporter (to the extent of 2000 tons), instead of a large importer of the oil of vitriol. In the year 1788 a great stimulus was given to the manufacture of sulphuric acid by Berthollet's application of chlorine (discovered in 1774 by Scheele) to the bleaching of cotton goods, rags, &c.; and still more in 1798 by the introduction of chlorine in the form of bleaching powder by C. Tennant & Co. of Glasgow.

The first acid chambers were erected on the Tyne in 1812, by Doubleday & Easterby. The acid was sold for 3*d.* per lb., and at that date the plan still adopted was to burn the sulphur and nitre together; but improvements had so far advanced that this operation was conducted in a separate furnace, and the gases evolved were conveyed by a pipe to the chamber. At that date however, there was no steam used in the chamber. They brought the acid up to about 70° or 80° Tw. (specific gravity 1·35 or 1·40), and then it was run off, and a fresh supply of water added to the bottom of the chamber. The produce of acid in these chambers was not more than 36 or 40 cwts., of specific gravity 1·80, from a ton of sulphur, or 180 to 190 per cent. (R. C. Clapham).

In 1821 Losh put up acid chambers at Walker, which were 25 feet long, 10 feet wide, and 10 feet high. The price of sulphur at that date had fallen to £7 per ton (the duty of £15 per ton having been remitted), and nitrate of potash was £32 per ton. Improvements had so far advanced that the nitrate of potash was decomposed by sulphuric acid, and a great saving was effected by the introduction of steam into the chambers, as suggested by Chaptel, which enabled a continuous working of the process to be carried on, and resulted in a much larger production of acid from the sulphur used. The strength of acid in the chamber was increased to about 100° to 120° Tw. The cost in these chambers at that time, with sulphur free of duty, was about £7 per ton. The sulphur was all imported from Sicily. The duty of £15 per ton was reduced in 1825 to 10*s.* per ton, and the price, delivered in England, was about £6 to £8 per ton. This state of things continued till 1838, when the then king of Sicily entered into an agreement with Taix & Co. of Marseilles for the exclusive sale of all the sulphur produced in his dominions. The effect was an immediate advance to £13 or £14 per ton, which was the cause of great depression and stagnation in the chemical trade. It was under these circumstances that the attention of chemists and manufacturers was directed to pyrites as a substitute for sulphur.

Sulphur Kiln.—Sulphur is still burnt in some works; a form of kiln which answers all the purposes required of it, and for which we are indebted to John Rilly of Hapton Chemical Works, is shown in Plate I. Fig. 1 shows the elevation, Fig. 2 longitudinal section, Fig. 3 plan. *a* is a cast iron funnel firmly fixed in the brickwork, and of the form of *a* (segment) Fig. 2. This funnel is filled with a definite amount of sulphur, which a rod prevents from descending too rapidly upon the iron-plate, *h*, on which it is burnt. *b* contains the sulphuric acid necessary for the solution of nitric acid gas from the nitrate of soda, which is placed in the cast iron dishes, *i i*. One of these dishes, *i i*, is charged at a time, and when completely used is withdrawn and emptied, whilst the other takes its place—a continual supply of gas being thus kept up. These dishes are inserted into the kiln by means of the doorways, *d d*, whilst the sulphuric acid is run upon them by means of the funnels, *e e*, seen in segment in Plate I. Fig. 2.

The sulphur being burnt on the iron-plate, *h*, the sulphurous acid gas passes in the direction of the arrows through the perforated brickwork, the draft being under complete control by means of the draft-hole, *c*. After passing through the perforated brickwork, it comes in contact with the nitric acid gas, which is being evolved from the iron-pots, *i i*, as seen in Fig. 2. The mixed gases now pass through another diaphragm of perforated brickwork by which they are more thoroughly mingled; from this they escape to the lead chamber by means of the chimney-flue, *g*.

Oil of Vitriol from Pyrites.—This mineral abounds in Cornwall and Ireland, and the first importation into the Tyne took place in 1840, by the late John Allan. MacTear states that Hill of London used pyrites as early as 1820. Perhaps nothing can give a more correct impression of the progress of chemical manufacture than the in-

creased production of sulphuric acid. From private sources the writer concludes, that not more than 200 or 300 tons of acid per annum were produced on the Tyne; and PARKER states that in 1815 not more than 5000 tons of acid were made in the whole of England. In 1830 the production on the Tyne had increased to 3300 tons, in 1876 to about 200,000 tons per annum; and the total production in all England, according to ROSCOE and SCHORLEMMER, had increased to 850,000 tons. (R. C. CLAPHAM).

The following analyses (taken from a large number) will show the composition of Cornish and Irish pyrites:—

CORNISH PYRITES.

Sulphur,	25·27	24·01	34·34	30·89	32·56
Iron,	27·77	32·67	32·20	32·67	30·71
Copper,	4·60	1·33	0·80	0·53	2·45
Zinc,	9·08	3·22	1·32	0·40	2·61
Arsenic,	0·71	trace	0·91	0·43	1·51
Silica,	31·06	38·67	29·00	33·33	27·15
Lead,	1·44	0·60	0·40	1·20	2·21
	99·93	100·50	98·97	99·45	99·20

IRISH PYRITES.

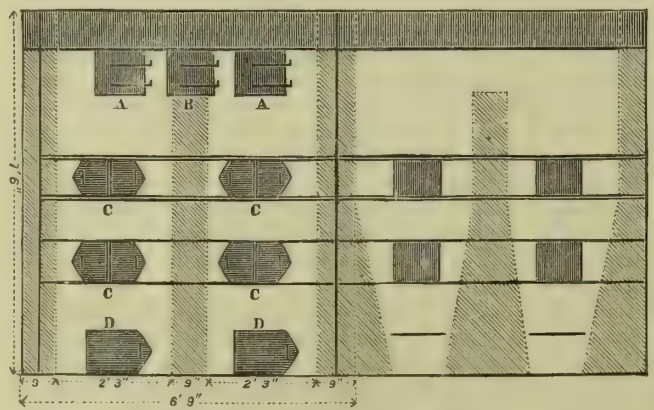
Iron,	32·22	35·00	34·65	42·40	41·50
Lead,	2·96	1·60	1·08	1·59	1·60
Copper,	4·13	2·40	2·40	1·33	2·50
Sulphur,	40·41	37·12	37·97	34·67	35·60
Zinc,	0·41	1·50	0·40	—	1·20
Arsenic,	0·71	1·60	0·40	0·18	1·40
Silica,	17·67	21·67	22·50	20·00	16·20
	98·51	100·89	99·40	100·17	100·00

(R. C. CLAPHAM).

Owing to the large percentage of silica in both classes of ore, it was found to be necessary that the kilns should be kept working at a moderate heat to prevent the ores from slagging up in the burners; and in consequence of this the burnt pyrites or "cinders" frequently contained from 4 to 6 per cent. of sulphur left unconsumed (as FeS and ultimately $FeSO_4$, 7 H_2O).

The following is the mode of burning these ores in 1845. Fig. 1 (Pyrites burners), shows a front elevation and section—A A, are the charging doors for pyrites; B, is the charging door for nitrate of soda; C C C C, are the poking doors; D D, are the doors for drawing the burnt ores.

Fig. 1.



The following are analyses of average samples of the "cinders," "burnt ore":—

	From Cornish Pyrites.		From Irish Pyrites.	
Silica,	27·00	18·50	30·50	30·64
Ferric oxide,	61·50	67·00	56·00	57·00
Sulphur,	4·12	4·67	4·76	4·20
Sulphuric acid,	3·43	3·54	2·97	2·74
Copper,	2·61	3·20	3·60	2·40
Lead,	1·20	1·30	0·51	1·60
Zinc,	trace	0·50	0·32	0·42
	99·86	98·67	99·66	99·00

(R. C. CLAPHAM.)

Foreign pyrites, imported from Spain, Portugal, Belgium, and other countries, soon superseded the English and Irish pyrites, chiefly owing to their much higher percentage of sulphur. Spanish pyrites were imported in 1856, Belgian in 1858, Westphalian and Norwegian in 1861. The cost of working the richer ores was found to be less, and the proportionate produce of acid was greater than with any of the English ores, and the smaller quantity of silica which the pyrites contained enabled the manufacturers to work the burners at a greater heat, and leave less sulphur in the cinders; and from the same cause the cinders became commercially saleable for the extraction of copper by the "wet method," while the ferric oxide ("Blue Billy") contained in the cinders became a valuable product for "fettling" in puddling furnaces, and in the making of pig iron.

The pyrites, from whatever source, contain arsenic in variable amounts, a part of which is deposited from the gases of the burners in the pipe leading to the chambers, and the remainder in the sulphuric acid, chiefly in No. 1 chambers.

The deposit in the burner pipe tested as under:—

	Clapham.	Smith.
Oxide of lead,	1·603	
Ferric oxide,	3·700	
Arsenious acid,	58·777	44·66—42·23—45·33
Sulphuric acid,	25·666	
Copper,	traces	
Oxide of zinc,	0·210	
Water,	8·000	
Insoluble, &c.,	2·333	
	100·289	

The following is an analysis of a sulphurous ore imported to the Tyrol from Milo in the Grecian Archipelago, in 1860, and used in making sulphuric acid:—

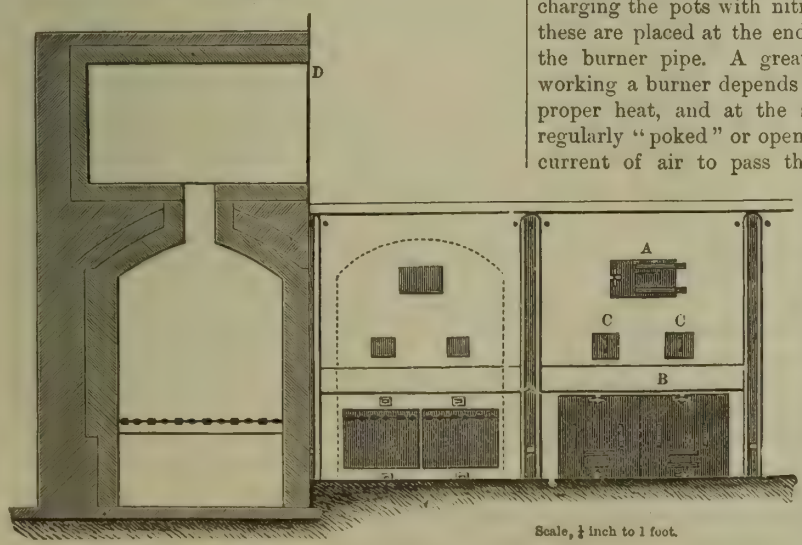
Sulphur,	24·00
Gypsum	62·20
Silica, &c.,	6·00
Water,	7·00
	99·20

Pyrites obtained from the coal measures are sometimes used, called "coal brasses," of which the following are an average analysis, after they have been partly freed from coal by the breakage of the ore:—

	Clapham.		
Sulphur,	40·50	.....	32·41
Iron,	46·35	.....	35·83
Coal,	7·90	.....	30·00
Silica,	1·55	.....	0·66
Carbonate lime and sulphate of lime,	4·00	.....	2·08
	100·30	.....	100·98

All pyrites imported into this country consists of large pieces or blocks; and before these can be used in the burners, it is necessary to have them broken to the size of road stones, which is effected either by an ordinary hand-hammer or by a Blake's crushing machine, the latter method being both more expeditious and less costly. By either method, however, as well as by the mere friction caused by the rolling of the vessel during transit to this country, and also in the loading and unloading of the cargoes, there is a considerable quantity of small or dust produced, which amounts to 10 or 15 per cent., and in some cases even more, according to the hardness or softness of the ores. The "smalls" are separated from the other parts by riddling, and are then ground in a pug-mill with a little water till the whole is in a pasty mass, when it is formed into "bricks" or "balls," which are dried by the waste heat of the burners; and it is found that, as a rule, the small per centage of sulphates of copper and of iron which exist in the pyrites from oxidation are quite sufficient to make the ground materials stick or adhere, so as to form a hard and compact "brick" when dried, and in this form they are well adapted for use in the burners. The broken pyrites and the "bricks" are then ready to be charged to the burners, and the usual method adopted, is best illustrated by the sketches, Figs. 2 and 3, of pyrites burners now in use:—

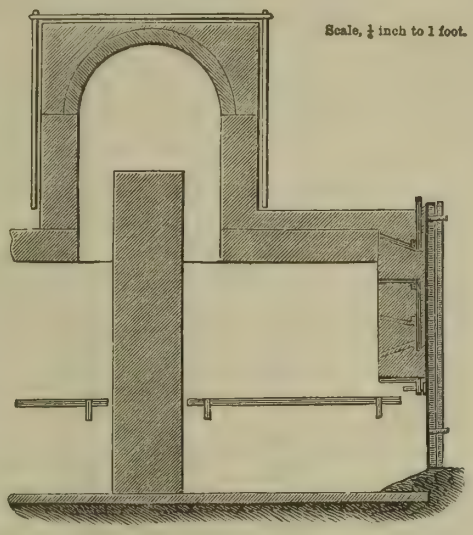
Fig. 2.



Scale, ½ inch to 1 foot.

Fig. 2, A, is the charging door of a burner which is about 4 feet square, and which can burn from 3 cwts. to 4 cwts. of ore each twelve hours. After charging, the ores are carefully and equally spaced over the surface of the kiln with a rake, and the door is then tightly closed. It remains for twelve hours, when the door, marked B, is removed, and the

Fig. 3.



Scale, ½ inch to 1 foot.

grates or bars upon which the burned pyrites rests are shaken by means of an iron bar made for the purpose; and this agitation causes the burnt ores near the kiln to fall between the bars, and they can then be removed to the depôt. The doors marked C are next opened, and the whole mass inside the burners is well stirred by means of a strong iron poker, and at the same time any "slags" which have been formed are removed. The burners are then ready for another charge of pyrites. The doors on the top of the burners, marked D, are for charging the pots with nitrate of soda. Sometimes these are placed at the end of the flue leading into the burner pipe. A great part of the success in working a burner depends upon its being kept at a proper heat, and at the same time properly and regularly "poked" or opened out, to allow of a free current of air to pass through the mass for the purpose of oxidising the sulphur and the metallic ores. The burned pyrites should be tested daily for sulphur, and when properly worked should not contain more than 2·5 to 4 per cent. of sulphur (calculated both from the FeS and the $FeSO_4$ and $CuSO_4$, &c.). If too high a heat is maintained, the ores are liable to "scar or flux," and to close up the burner, and in some cases the nitrate of soda is decomposed too rapidly to be useful, or the gases

may even be reduced to nitrogen monoxide and nitrogen, which are useless in the chambers.

The following are analyses of Spanish and Belgian pyrites:—

SPANISH PYRITES (THARSIS).

	Clapham.				(M'Culloch). Mason's.
Sulphur,	45·21	47·50	43·52	48·11	49·80
Iron,	43 50	41·92	46·20	40·20	42·80
Lead,	0·22	1.52	2·11	2·20	—
Zinc,	—	0·22	0·32	0·81	0·10
Copper,	2·21	4·21	3·12	3·11	2·26
Arsenic,	0·41	0·38	1·10	1·21	0·28
Silica,	7·10	3·42	2·00	2·26	2·94
Water,	1·21	0·56	1·54	1·00	0·95
	—	—	—	—	0·18 *
	99.86	99·66	99·91	99·00	99·36

* $CaCO_3$.

	Belgian Pyrites. (Clapham).		Norwegian. (M'Culloch).
Sulphur,	42·80	35·50	46·15
Iron,	36·70	38·60	44·20
Ferric oxide,	7·23	4·24	—
Lead,	0·92	0 65	—
Zinc,	0·40	5·26	2·10
Arsenic,	0·20	0·31	trace
Silica,	8·86	14·90	3·20
Carbonate of lime,	0·84	trace	2·55
Water,	1·46	0·56	0·40
	—	—	1·20 Copper
	99·41	100·02	99·80

The mixed gases from sulphur and nitre, as they leave the burners, are conveyed through a large metal pipe lined with bricks to the Glover's tower, or denitrating tower, which will be explained hereafter, and from thence to the chambers, where they come in contact with a due supply of steam. According to theory, 100 parts of sulphur should give 306 parts sulphuric acid; but in practice this result is not obtained, as some sulphurous acid is almost necessarily lost in the gases escaping from the chambers, and, as has already been stated, there is 2½ to 4 per cent. sulphur left in the burnt ores. Many manufacturers calculate on 290 to 300 parts pure acid from 100 sulphur used, so that there may be about 570 of sulphur actually lost; but only part of this passes away into the air. Dr. Smith, in his report for 1871, gives the result of an examination of twenty-three chemical works, which show an average escape of 7·606 per cent.; but this includes several very imperfectly managed works. In well-conducted works the escape is not more than 1·5 to 2·5 per cent. on the average.

Chambers.—It has been shown in a former part of this article that the sulphuric acid chambers at the early stage of their construction were of small dimensions, say only 12 feet long, 10 feet broad, and 6 feet high; of late years they have been made very much larger, both as to length and height; in some cases 200 feet long, 30 feet broad, and 30 feet high. But it is not at all satisfactorily demonstrated yet, whether the excessively large chambers which are sometimes now put up in Lancashire are any real improvement on the more moderate size of 100 feet long, 20 feet broad, and 18 feet high, and worked in a series of four or six chambers together. A chamber of the above dimensions has a working capacity of 36,000 cubic feet. The first chamber of a series (No. 1) is usually constructed of 7 lbs. lead, and the other chambers (Nos. 2, 3, 4, and 5), are made with 5 to 6 lbs. lead. The wear and tear of the chambers depends on the quantity of pyrites which is burned for each 100 cubic feet of space, and the degree of heat which is maintained in them. No. 1 chamber usually requires rebuilding in three or four years; but the other chambers in the series may be expected to last from five to seven years, or even longer. When any of these chambers are taken down at the end of the times named, a large quantity of sulphate of lead is found at the bottom of the chamber, caused by the action of nitric acid on the sides and top of the chamber, and which is nearly equal in weight, when smelted, to the loss of lead. This precipitate is dried and furnaced, and then sold to the lead smelter. Each chamber is supplied with a glass float to show the depth of acid in the chamber, and a hydrometer and thermometer are used to give the strength of the acid and heat of the chamber. In all well regulated works the production of acid is carefully ascertained at frequent intervals.

When pyrites testing 47 per cent. sulphur are used, the production of sulphuric acid, specific gravity 1·848 (170° Tw.), should equal 132 to 136 parts from 100 parts of ore. The practical results, however, vary in accordance with the construction and arrangement of the burners and the chambers, the draught, the supply of steam, and the heat. Although we are indebted to the labours of Clement-Désormés, Davy, Provostaye, Peligot, and others, for much theoretical knowledge on sulphuric acid making, still there is a wide field open for the investigations of the rising generation of chemists. The late H. A. Smith recently made many careful experiments in this direction. The chamber in which the trials were made was a large Lancashire chamber 140 feet long, 30 feet high, and 25 feet broad; and the object in view was to ascertain at which part of the chamber the largest production of acid took place. The tests were made at 3 feet from the bottom and at 15 feet from the bottom—one being below and the other above the entrance pipe for the gases from the burners, and at every 10 feet in length of the chamber. In the first experiment the amount of sulphurous acid was examined, in the second the amount of sulphuric acid, and in the third the amount of nitrous acid.

(1). *Sulphurous Acid, 3 feet from bottom.*—At 10 feet from the entrance the sulphurous acid was only 3 per cent. (which was the highest point), and from thence it decreased till, at 130 feet, it fell to 8 per cent.

(1). *Sulphurous Acid, 15 feet from bottom.*—At 10 feet from the entrance there was 72 per cent. of sulphurous acid, and this continued for another 10 feet. There was then at 30 feet a rapid fall to 46 per cent., and at 40 feet to 31 per cent.; and after this the variations were not so marked, and the sul-

phurous acid became less and less, till its lowest point was reached at 120 feet, where it was 13 per cent.

In the experiments at 3 feet from the bottom the differences are not so great as at 15 feet from the bottom, the latter being more affected by the steam entering the chamber, which, as far as could be determined, was equal to about one-quarter of the mixed gases. This result appears to show that the upper portion of the chamber is chiefly used as a reservoir for sulphurous acid, whence it descends to the working portion of the chamber, next the acid at the bottom, for condensation as sulphuric acid. This was checked in another way, by placing a collector in the chamber at 4 feet from the bottom, and at 16 feet from the bottom. From the former there was a regular and fairly large make of acid; but from the latter there was scarcely any production, there being only one-sixteenth of an inch after standing nine days.

(2). *Sulphuric Acid*, 3 *feet from bottom.*—Beginning at 10 feet from the entrance the acid was 81 per cent., then a sudden rise brings it to 89 per cent. at 20 feet from the entrance, after which the percentage falls regularly till at 100 feet the quantity is 30 per cent., and it remains nearly at this to the end of the chamber.

(2). *Sulphuric Acid*, 15 *feet from bottom.*—At 10 feet from the entrance there is no sulphuric acid, and this is the case up to 140 feet, with very little variation. The highest is reached at 50 feet, where it is 23 per cent.; on the whole showing very little production at this height compared to the 3 feet from the bottom, where the acid was in marked contrast. In the sulphurous acid experiment the largest amount is at the top of the chamber, and the smallest at the bottom; but in the sulphuric acid experiment the largest amount is at the bottom, and the smallest amount at the top.

Nitric Acid.—The variations were found not to be so marked as in the above, the differences being between 3 per cent. and 26 per cent. At 100 feet from the entrance it was highest, and at 140 feet it rapidly sank to 3 per cent.

H. A. SMITH concludes that a chamber should be divided into two parts, the working portion and the reservoir for the stock of gases; and that if the height of the chamber was lowered, and at the same time its length was increased, we should have a better condensing surface, as most of the acid appears to be produced next the already formed acid at the bottom, and he suggests as a good size for a chamber, to have it about 150 feet long, 25 feet broad, and 12 feet high.

The heat at which a chamber is worked is an important part of the operation of an acid-maker, and it is generally admitted that, to do well in the production of acid, the working part of the chamber should never be below about 200° Fahr. Under that heat little or no production takes place; a fair working heat may be considered to be about 220° Fahr. This applies especially to the lower regions of the chamber; but the upper part, nearer the roof, is seldom or never so high, and ranges from 120° to 150° Fahr. Many of these results, however, as to heat and production, depend very much upon the size of the chamber and the way it is worked; and some manufacturers believe that *surface* as well as space has much to do with the rapid and large formation of sulphuric acid. WARD took out a patent for the use of sheet-glass, which he placed in a chamber 200 feet long, 3 feet high, and 3 feet wide, and each sheet was placed about 1 inch apart, so that the mixed gases passed between the damp sheets of glass and were rapidly condensed. Steam was introduced at certain points, so as to produce an acid standing about 135° Twad. (specific gravity, 1·675), which contained a good deal of nitrous acid, and was all taken to the Gay-Lussac denitrating column, to free it of its nitrous fumes. The patentee claimed for his method a greater make of acid in a given space, a larger production of acid from a given weight of pyrites, a smaller quantity of nitrate of soda, and the wear and tear of the chamber reduced. This class of chamber was tried on the Thames by the late T. BELL, but has not come into general use.

In 1844 a great saving was effected in the manufacture, by the adoption of GAY-LUSSAC'S process for the recovery of the nitrous compounds, which had hitherto been allowed to escape into the air and were wasted. This important improvement consisted of absorbing the nitrous gases by means of strong oil of vitriol. It was introduced into England by DE COURCY; and its adoption has lead to a decrease in the consumption of nitrate of soda, equal to more than one-half of the quantity formerly used. The method which is usually adopted in chemical works is as under:—The whole of the hot sulphurous gases from the burners is made to pass under and over a metal pot inclosed in tight brick work, in which is placed a charge of nitrate of soda and sulphuric acid. The length of time required to decompose the nitre depends on the weight used; but the pot is usually run off every three or four hours, and a fresh charge is made to enable the supply of nitrous fumes to the chamber to be continuous. Fig. 4 is a section of one of the nitre pots now in use:—

Fig. 4.



The sulphate of soda formed from the decomposition of the nitre is in a semi-fluid condition, and is run off from the pot by means of a plug, P; and after cooling, is broken up and used in the soda process. The analysis is as under:—

Sulphate of soda,.....	81·25
Free sulphuric acid.....	17·10
Salts of lime, iron, &c., ...	1·75
Water (uncombined),.....	0·50
	100·60

The mixed gases from the burners pass along a large metal pipe lined with fire bricks to a lead tower, called a denitrating column, or Glover tower (shown in Figs. 5, 6, and 7), and constructed of lead about 14 lbs. to 31 lbs. to the foot, and say about 20 to 25 feet high × 10 feet square. This tower is filled with bricks or fire-clay blocks to a certain height from the bottom, and then with flints or hard coke to within about 2 feet of the top. The hot gases from the burners, standing about 350° Fahr., pass into the column at *a*, and are met by a stream of nitro-sulphuric acid from the Gay-Lussac absorbing column (which it thoroughly denitrates), and also a stream of weaker acid from the chambers; the gases finally pass into the vitriol chambers, considerably cooled, by the flue, *b*. It is usual to have two cisterns for the supply of the acid —one to contain the nitro-sulphuric acid, and the other the weak acid. The two streams of acid are made to meet on entering the top of the column, and the weak acid assists in liberating the nitrous fumes held in the stronger acid, and each acid is in turn concentrated on its way through the column, and runs out at the foot at about 150° T. (1·750 specific gravity), and after cooling is again available for the absorption of more nitrous acid. The weak acid referred to above, the sulphurous acid, and the heat in the column, all act together in separating from the strong acid from the absorbing column its nitrous gases for use in the chamber. The acid is cooled by causing it to run through a long coil of lead pipe about 2 inches in diameter, which is placed in a trough, through which continually pours a running stream of cold water. Another advantage derived from this tower is, that all the evaporated water is economically employed as steam in the chambers.

Fig. 5.

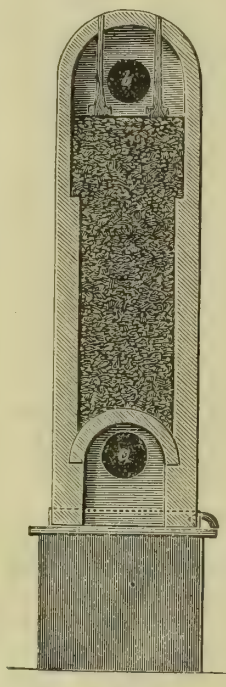
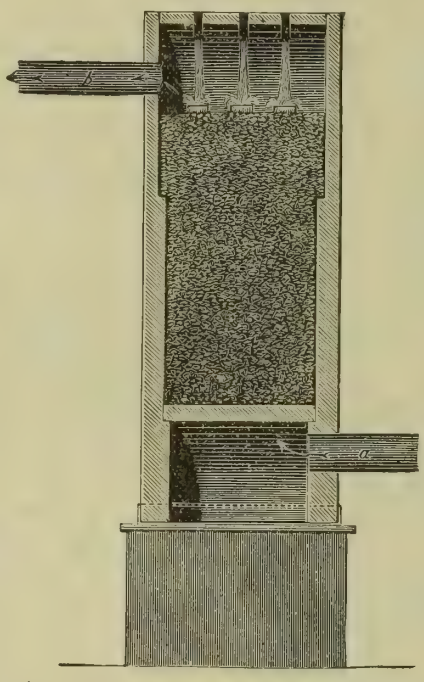
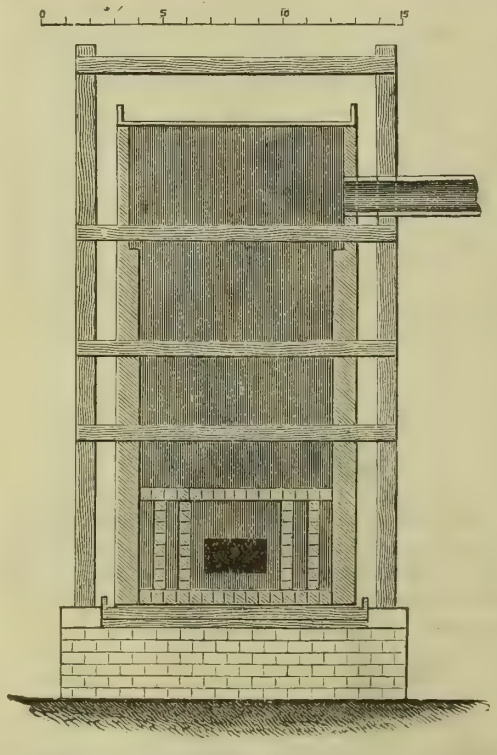


Fig. 6.



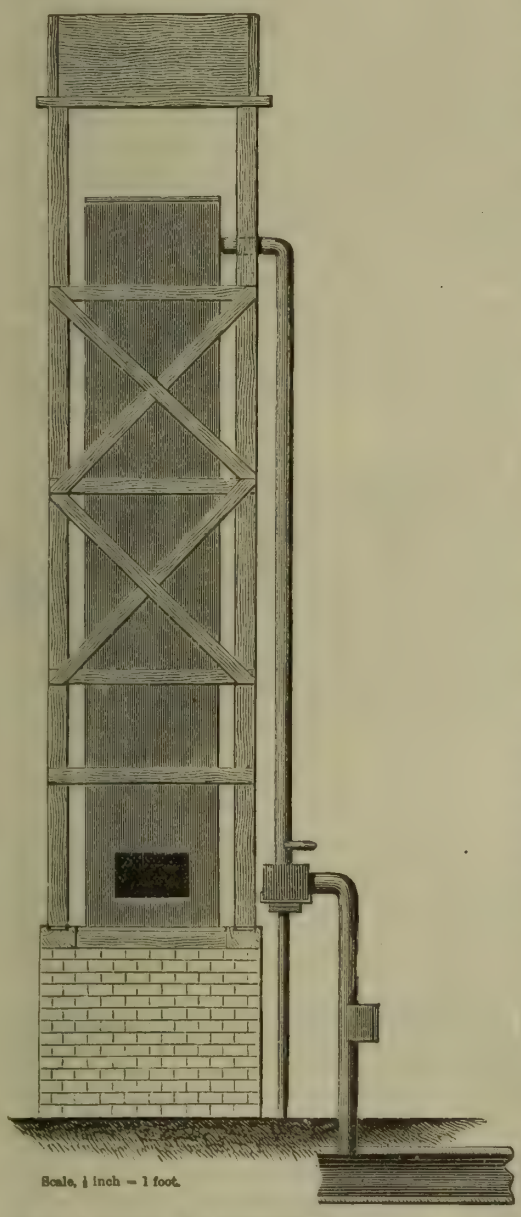


The nitrate of soda used at the burners, with a well-regulated Gay-Lussac apparatus at work, need not be more than 1·75 to 2 per cent. when using pyrites testing about 47 per cent. of sulphur, or about 3·72 to 4·25 per cent. on the sulphur in the ore; whereas, before the Gay-Lussac apparatus was used, the nitrate of soda was about 4 per cent. on the former and 9 to 10 per cent. on the latter. With all the care taken, however, a certain weight of nitre, or its equivalent in nitrous acid, is almost necessarily lost. This loss varies in different works, but may be said to be from 3 to 6 per cent.; and the chief sources of loss occur in the acid on the floor of the chamber, which absorbs some nitric oxide from a small escape at the exit pipe of the Gay-Lussac column, already referred to, and a small waste at the burners. The Glover tower is sometimes so placed that the nitro-sulphuric acid from the Gay-Lussac tower, and the weak acid from the chambers, will both run to it without pumping, and are mixed as they enter together at the top.

The final stage in the operations connected with

the acid chambers is the absorption of the nitrous acid fumes as they escape from the last chambers of the series; and at this point it is expected that all, or all within a small trace of the sulphurous acid, has been obtained as sulphuric acid in passing through the chambers. The last chamber (we will suppose to be No. 6 in the series) should have its

Fig. 8.

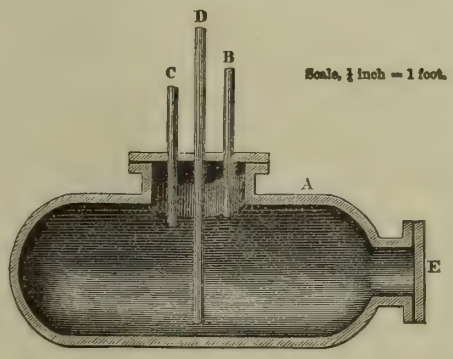


gas kept always of a reddish-brown colour, and the "drop" from the last pipe leading to the Gay-Lussac column should be about 90° or 100° Tw. The column in which this important operation takes place is called an "absorbing column," and is usually constructed about 40 or 50 feet high, 6 feet square, and of 10 lbs. to 14 lbs. lead. An escape pipe for draught leads from near the top to the flue or chimney; a cistern is placed above all, which holds a supply of cold and strong sulphuric acid, standing about 150° Tw., and the supply of acid to the column is regulated by a "catch siphon" or "tumbling box," which maintains a regular and continuous supply of acid. The nitrous acid fumes are absorbed by the strong acid, and the gas which at last escapes to the flue should show no trace of colour. The amount of escape may be tested very accurately by J. MacTear's method, as described under Hydrochloric Acid, and which is equally applicable to this purpose. Fig. 8 is an elevation of a Gay-Lussac absorbing column.

The column is 30 feet high × 6 feet square, and filled with hard burnt coke. The cistern on the top supplies the strong acid, as already explained.

Sulphuric acid is pumped up to the cisterns by means of compressed air, and the arrangement is well illustrated by the sectional drawing, Fig. 9.

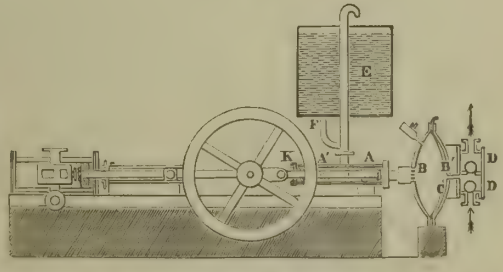
Fig. 9.



A is a metal vessel 2½ inches thick, 6 feet long, and 3 feet diameter, into which the acid is run, and which holds 57¼ cubic feet of acid, or about 300 gallons. B is a pipe through which the supply of acid is received into the vessel. C is the air pipe through which the compressed air is forced from the engine. D is the exit pipe which conveys the acid to the absorbing column. E is a door or manhole to enter the vessel for repairs, &c.

An excellent acid pump, invented by George S. Hazlehurst, is shown in Fig 10. It is in use at

Fig. 10.



his works at Runcorn, and pumps acid nearly 50 feet high. A A′, an ordinary water pump barrel; B B′, two saucers of cast iron, with india rubber

diaphragm, C; D D, india rubber ball valves; E is a water tub connected with A′ by F. As the ram works backwards and forwards, the diaphragm, C, waves to and fro, drawing and forcing the acid through the valves, D D; at each *back* stroke the water in A′ shoots up the pipe and delivers into the top of E; at each *front* stroke the water fills A′ from the bottom of the tub, through F. Thus the water is constantly changed without any valves whatsoever: this circulation is necessary because of the inevitable entanglement of air passing through gland K. The feed cistern may be placed either below or above the pump: in the latter case an air vessel is required on the suction pipe. Of course, all necessary parts are lined with india rubber. By this means weak acids from wash towers may be profitably re-pumped, and in some cases more than half the water saved, more bleaching powder made per ton of salt, and a source of pollution of streams avoided.

A point of some importance in connection with the economizing powers of the Gay-Lussac column, is the regularity of the stream of acid which runs down. This is secured by a valve attached to a float in a subsidiary feed cistern, so arranged as to keep the acid at one level.

The quantity of sulphuric acid used in the Gay-Lussac tower is rather variable, some manufacturers being more successful in this respect than others. Many who employ this apparatus recommend one-third of the make to be run down every twenty-four hours. In this case, for every 100 tons of acid made per week, nearly 5 tons would be run down per day. One manufacturer finds in practice that about 400 gallons, or 7000 lbs., run down the column every twelve hours, will absorb the nitrous gas from a set of chambers which are converting 18 tons of sulphur weekly into sulphuric acid.

Chamber Reactions—The theory of the formation of sulphuric acid in the chambers has occupied the attention of many learned chemists. Clement-Désormés was amongst the first to trace the complicated reaction in the lead chambers. He showed that nitric acid vapour and sulphurous oxide, when mixed, react on each other in the presence of moisture in the form of steam, and thence follows the formation of sulphuric acid. The nitric acid parts with oxygen and becomes nitrogen tetroxide ($N_2O_5 = N_2O_4$ (or $2NO_2$) + O). The reaction continues however, oxygen is parted with, and the tetroxide becomes nitrogen dioxide, or nitric oxide ($N_2O_4 = N_2O_2$ (or 2NO) + 2O). Nitrogen dioxide N_2O_2 is reoxidised by the atmospheric air, which is always present in a chamber, into nitrogen tetroxide N_2O_4, and becomes available again for further action on the fresh supply of sulphurous acid gas from the burners. The crystalline substance, so often referred to by older chemists, $= (2N_2O_3, 2H_2O_3)\ 5SO_3$,* always appeared in the absence of a proper supply of steam, but was instantly decomposed by more water into sulphuric acid, nitrogen dioxide, and nitric acid. Clement-Désormés ascertained that the action continued either till the sulphurous acid or the oxygen of the air became exhausted, and he verified this proposition as to what occurred in the chambers by mixing in a glass globe three gases (nitric and sulphurous oxides, and air). The immediate production of red vapour showed the formation of nitrogen tetroxide (NO_2); and now the introduction of a very little water caused the proper reaction, and opaque vapours were seen, which deposited white crystals on the surface of the glass. The gases were then colourless; but on another addition of water the crystals melted with production of ruddy vapours. The same chemist tried important experiments on the requisite heat for the above reactions. He took a glass globe, into which was placed a piece of ice, and which was furnished with three openings; into one was passed sulphurous acid gas, and into the second nitrogen dioxide, and into the third oxygen. The globe was kept cool by being immersed in iced water. No sulphuric acid was formed; but on exposing the same to a heat of 100° Fahr., the gases began to react on each other, and sulphuric acid was produced. These facts are now well-known to practical manufacturers.

The formation of sulphuric acid in the leaden chambers may be simply expressed by saying that although sulphurous oxide (SO_2) in presence of water or steam is unable rapidly to absorb atmospheric oxygen, it is able to take up oxygen from such combinations with nitrogen as N_2O_5 or N_2O_4. If these oxides are formed in the chamber they give up part of their oxygen to the sulphurous acid, and are reduced to nitrogen dioxide (N_2O_2). This gas is, however, able to absorb free oxygen, and is at once reconverted into N_2O_5 or N_2O_4. This continuous reaction may be represented as follows:—

$$(1.)\ NO_2 + SO_2 + H_2O = H_2SO_4 + NO.$$
$$(2.)\ NO + O = NO_2.$$

It is thus clear that nitrous fumes act as a carrier between the oxygen of the air and the sulphurous acid, so that theoretically an infinitely small quantity of these fumes will be sufficient to cause the combination of an infinitely large quantity of sulphurous acid, oxygen, and water to form sulphuric acid (Dr. Roscoe).

Practically, however, this is not the case, because instead of pure oxygen, air must be used, and four-fifths of this consists of nitrogen, which so dilutes the other gases that in order to obtain the necessary action a considerable quantity of the oxides of nitrogen must be added; and as this nitrogen must be removed from the chamber, it necessarily carries with it a large quantity of the nitrous gases, which are dealt with as already described.

In producing acid in the chambers it takes about 220 parts of water in the form of steam, to convert 100 parts of sulphur into sulphuric acid. Sprengel has suggested the use of a jet of water in the chambers in the place of steam, as less costly; but it has not yet come into general practice,

* De la Provostaye has shown the existence of a crystalline compound having the same properties containing $N_2O_3.2SO_3$.

and has the disadvantage of not at the same time adding heat to the chamber, which is done by steam.

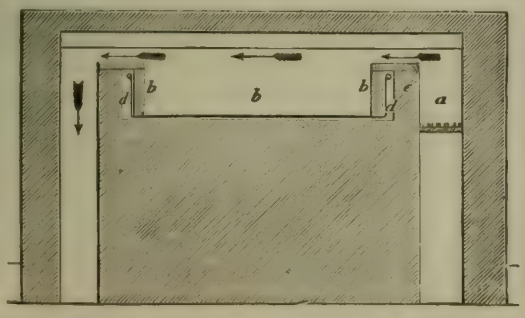
Concentration of Sulphuric Acid.—Sulphuric acid is concentrated in leaden pans until it has attained the specific gravity of 1·750; beyond this point it is not considered safe to push the concentration in lead. In order to bring it up to its maximum degree of concentration, it is rectified in vessels of glass or platinum.

With respect to its concentration in lead, a variety of plans are in use for this purpose. Much difference of opinion exists on this head amongst sulphuric acid manufacturers; their choice probably depending on convenience and situation. Alkali makers prefer to concentrate the vitriol by passing the flame and products of combustion of a reverberatory furnace over the surface of the weak acid, &c.; but as the concentrated acid resulting from this mode of working is almost invariably very black and turbid, such acid does not suit calico-printers, bleachers, and other such consumers.

The following describes the plant of a manufacturer who makes for sale only. It consists of two pans, placed side by side, one being placed so much higher than the other that its contents can be emptied completely by means of a siphon into the lower pan. Each pan must be formed out of one solid sheet of lead, the sides and ends being simply turned up: the lead is half an inch thick, the other dimensions of the sheet being 33 feet by 7 feet 6 inches. These pans are bedded on brickwork, and heated by flues passing beneath them; but they are protected from direct contact with the flame by a course of fire-tiles and, at a greater distance from the fire, iron plates.

The mode of working is as follows:—The vitriol in the lower pan being of the proper strength, the workman proceeds to run it off into a vessel called a cooler, where it remains until cold. He runs it empty to within 2 or 3 inches; when this is accomplished, he proceeds to set a siphon into the upper pan, running the contents into the lower one, which he fills to within 2 or 3 inches of the top. When the upper pan is empty he refills it with the weak acid from the chamber; he then proceeds to fire the pan until next day, when he will repeat the operations just described.

Fig. 11.



A surface concentrator, in vertical section lengthways, is shown at Fig. 11, the fireplace is at *a*, the flame proceeding in the direction of the arrows over the surface of the dilute acid at *b*, when it descends into the flue, carrying with it the evaporated water; *d d* is a section of the leaden pan. The lead is protected from fusion by being inclosed in brickwork. The side of the pan is brought up to the furnace dam, *e*; and within it a close row of firebricks, *b*, are placed on end, but not cemented in any way. Thus the sides of the pan are inclosed between brick walls; it only remains to cover up the space, and this is done by placing firebricks on the top, resting partly on the furnace dam, and partly on the rows of bricks just mentioned. Some manufacturers employ covering bricks, expressly made for the purpose, with an indentation or channel formed in them; this channel being for the purpose of inclosing the upper edge of the pan.

The lead of which vitriol pans are made is in some cases one inch thick. They are covered in by an arch of firebrick, through which a hole is pierced over one corner of the pan; through this hole the pan is filled and emptied. Samples are taken from time to time, cooled, and tested with the hydrometer. When finished it must be of the density of 1·750, or of the strength of 150° Tw., when at a temperature of 60° Fahr. When of this density, the fire is drawn and the vitriol run into shallow lead vessels almost identical with the first-described pans, formed out of an entire sheet of lead, sometimes half-inch, often of quarter-inch thick. These "coolers" are set on iron plates in the manner described with reference to the upper pan; but the ends of the flues are open to the air, which, circulating through these passages, carries off the heat. The sides and ends are held up by brick walls or other convenient supports.

Very good and efficient coolers are constructed of cast-iron plates lined with quarter-inch lead. The lead must be turned over the upper edge and flattened down so as to prevent any infiltration of acid between the iron and the lead. They are set on two low brick walls, so that almost the whole surface of the iron is exposed to the cooling influence of the atmosphere.

The system just described is not by any means universal, each manufacturer arranging his apparatus according to his wants.

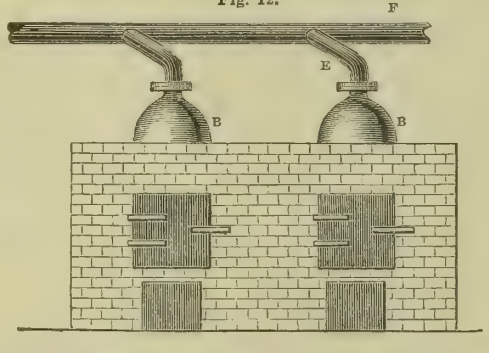
The sulphuric acid thus made is called brown oil of vitriol; its colour is due to a certain amount of organic matter which finds its way into it, and which, subjected to the joint action of the acid and heat, becomes carbonized, and colours the whole of a dingy-brown hue. If the colour is too strong, it is usual to destroy it by sprinkling a small quantity of some highly oxidizing body into the vitriol while hot in the pan; either nitrate of potassium or sodium answers well for this purpose. Finely powdered black oxide of manganese may be used.

Sulphuric acid of commerce invariably contains lead and arsenic. Lead always makes its appearance as sulphate when strong acid is diluted with water, the concentrated liquid being able to dissolve a portion of this salt which, when diluted, it is not

able to retain. Nitrous compounds also are found, together with traces of hydrochloric acid. Traces of selenium have also been detected. Arsenic is a common impurity, derived usually from the iron pyrites. Traces of arsenic, too, have been detected even in vitriol made from commercial sulphur. For the great majority of purposes these impurities are not found inconvenient in the arts; while, on the other hand, for some special uses a process of purification must be had recourse to.

Sulphuric Acid—*Rectified Oil of Vitriol—English Oil of Vitriol.*—It has been stated previously that the concentration cannot be safely conducted in lead beyond the density of 1·750. The further concentration, then, must be performed in vessels made of a material which will withstand the corrosive action of the boiling acid, and which is comparatively infusible. Glass at once suggests itself or some variety of earthenware, such as porcelain, or, amongst the metals, platinum or gold. Of the former two glass offers most advantages; and of the two latter materials platinum is preferable, inasmuch as it resists acids quite as well, and is much cheaper than gold. Glass has been employed in the concentration of vitriol from very early times, perhaps from the period when sulphuric acid began to be understood, and its manufacture attempted on a very small scale, doubtless before the introduction of leaden pans. Platinum, on the other hand, is a comparatively late introduction. The glass vessels employed in the last concentration of sulphuric acid, or, as they are technically known, retorts, resemble very much the bottles or carboys used to transport vitriol from place to place. Fig. 12 represents the

Fig. 12.



whole arrangement when at work. The retorts vary in size; those in use at the present day are capable of holding more than 20 gallons of liquid.

The mode of working can be gathered from the drawing, where A represents the fireplace; the flame from the fire plays round a cast-iron pot, finally making its exit into the flue. On the bottom of the iron pot just mentioned a quantity of dry sand is laid; and on this the retort, B, is placed, the sand serving as a steady support for it. The retort is not, as is sometimes supposed, surrounded with sand; for, if this were done, it would run some risk of being broken, besides materially retarding the cooling when the rectification was over.

The retort being placed, as in the drawing, it is filled with warm brown vitriol, and when this is done the fire is lighted; the arm, E, is put into its place; eventually the acid boils; water, with a little sulphuric acid, distils off. The vapour passes off by the stoneware arm, E, into the leaden draught-pipe, F, where a quantity of it condenses; but the greater portion finds its way from thence into the chimney. The contents of the retort are kept boiling for some hours, or until the brown colour entirely disappears; for this appears to be the only reaction by which to determine the conclusion of the rectification. It would appear that the organic matter resists the destroying or oxidising action of the acid, until it has reached its highest point of concentration and temperature. When the clearing has taken place, the fire is withdrawn from beneath the pot; and the whole arrangement is allowed to cool down to a safe temperature, when it is drawn off in carboys. This drawing off is effected by a siphon, with the shorter of its two legs turned back upon itself. In order to withdraw the concentrated acid from the retort the workman first removes the earthenware arm; the siphon is filled with water, the man keeping his thumb firmly closed over the orifice of the longer leg. The shorter leg is inserted into the retort, and gently placed on the bottom; the workman then removes his thumb for a few seconds, until the acid has driven before it the water with which the siphon was charged; when this is done, the end is directed into a carboy which has been placed in readiness by an assistant. When the carboy is full the orifice is again closed by the thumb, while the full carboy is removed and replaced by another empty one. The whole range of retorts are emptied in this manner.

The product is the strongest English sulphuric acid; it is colourless or nearly so, and is of the density 1·850, or 170° on Twaddell's hydrometer.

In 1871 an entirely new process was devised by Junius Gridley of New York, and was patented in this country as a communication by Henry Chance, of the firm of Messrs. Chance Brothers, & Co., of Birmingham. To the ordinary system of working with glass retorts, unconnected with each other, in which the rectifying is commenced, continued, and finished in one retort (as described above), there exist many objections. The acid in each individual retort, after being rectified, has, together with the surrounding brickwork, to be cooled down before it can be drawn off into carboys. This necessitates a large consumption of coal in reheating the brickwork each time the retort is filled with crude acid. In bringing the acid to the boiling point at the commencement, and in cooling it down again at the close of the operation, the very greatest care has to be taken to avoid breakage; while the liability to accident, and the labour required in filling and emptying each retort, are material objections to the process.

Under the new system these difficulties are obviated by making the process continuous. The retorts are set in beds of four each. They are arranged, as shown in Fig. 13, on different levels, and are

connected together by tubes of glass, as will be shortly described. A constant stream of acid from the leaden concentrating pans is run, by means of a leaden pipe, into the topmost retort of the series, the supply being regulated by a tap. After undergoing a certain degree of concentration in this retort, the acid flows through the glass tube into the retort next below; and so on through each succeeding retort of the series, undergoing a further degree of concentration in each, until it leaves the lowest in a continuous stream of fully concentrated acid. After passing through a leaden cooler placed in a trough of water, the acid runs direct into the carboys and is ready for delivery.

Fig. 13.

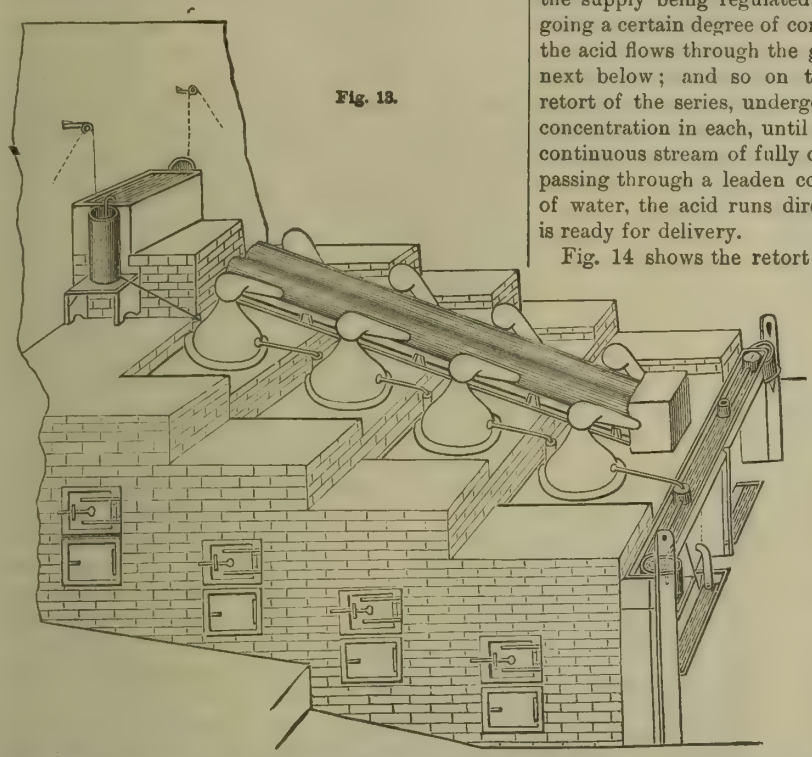
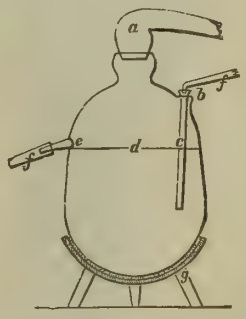


Fig. 14 shows the retort used in detail. *a* is the glass head for conveying the mixed vapours of acid and water to the draught-pipe; at *b*, in the shoulder of the retort, there is an opening through which the funnel, *c*, passes, and by which the acid enters the retort; *d* shows the level of the acid; *e* is the tubule attached to retort, by which the acid leaves retort; and *f f* shows the glass connector which conveys the acid from one retort to another. The retorts are set in sand, in shallow iron pots, *g*.

Fig. 14.



The strength of the acid is regulated by increasing or diminishing the supply from the acid pans, and is under constant supervision as it flows into the carboys, thus obviating any possibility of error as to strength.

The escaping mixed vapours of acid and water are conveyed by the draught-pipe to small leaden towers packed with coke, and are there condensed.

Four beds of retorts, *i.e.*, sixteen retorts, will produce from six a.m. on Monday till twelve noon on Saturday, 600 carboys, equal to 46 tons. For this, the labour required consists of two retort men (day and night turns), and two labourers. The retort man on each turn has the charge of the retorts; the labourer attending to the concentrating pans, wheeling coals and ashes, and removing the finished acid.

Taking the result of many months' working, the average consumption of coal is 28 lbs. per carboy of 175 lbs.

There being no loss of heat in the repeated cooling and re-heating of the brickwork which are necessary under the old system, and no labour required in filling and emptying retorts, coal and manual labour are reduced to a minimum.

This process has for some years been in most successful operation in nearly all the vitriol works in the United States, and is now being largely adopted by manufacturers in England.

A platinum retort, with its appendages, is shown in Figs. 15 and 16. The former is a vertical section in front; *a*, is the body of the retort; *b*, the head; *c*, a platinum tube leading from the head to a leaden worm, which worm is kept immersed in water; *e*, is a platinum funnel, the tube of which is S-shaped, to prevent the return of any vapour. The brown acid which is kept in the cistern, *f*, under which the waste heat passes, is run into the body of the retort without the aid of any tap or valve by means of the at-first sight rather complicated, but really simple apparatus shown in the figure, where *g* represents a round vessel in which a tube, *h*, is inserted very near to the bottom; *i*, is another leaden vessel, which has a slit in the side from the top nearly to the bottom, along which slit the tube, *h*, slides, when the vessel, *g*, is moved up or down by means of the chain and pulley. A siphon, which is kept constantly set, connects the stock cistern, *f*, with the vessel, *g*. The apparatus when in the inactive state, as represented by the dotted lines, is as follows:—The siphon is full of vitriol, but the surface of the acid in the cistern being on a level with that in vessel *g*, no flow can take place. When

the vessel, g, is lowered, the levels become altered; and as the leg of the siphon, which is in vessel g, becomes the longer, the acid begins to run into this vessel, and from this into vessel i, and thence into the funnel.

The other portions of the apparatus being at the back, are shown in Fig. 16, which is a side view; a, as before, is the body of the retort; b is a platinum tube about three-fourths of an inch in diameter, in

Fig. 15.

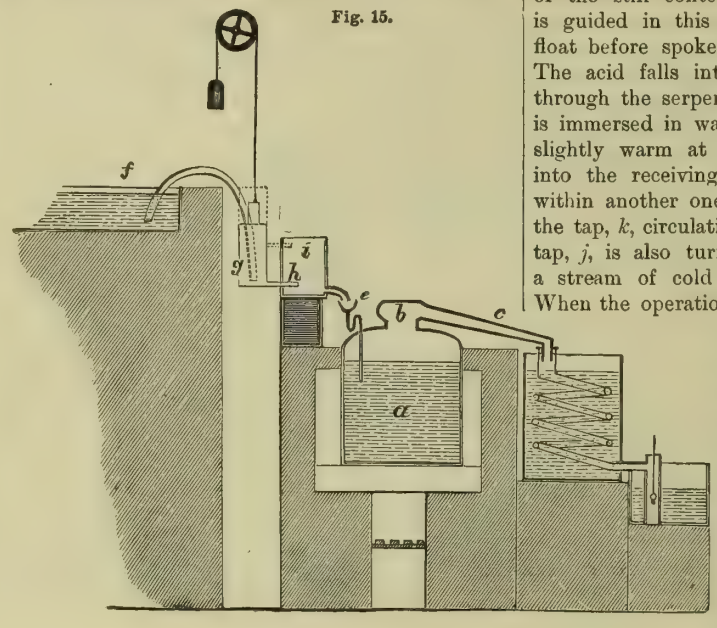
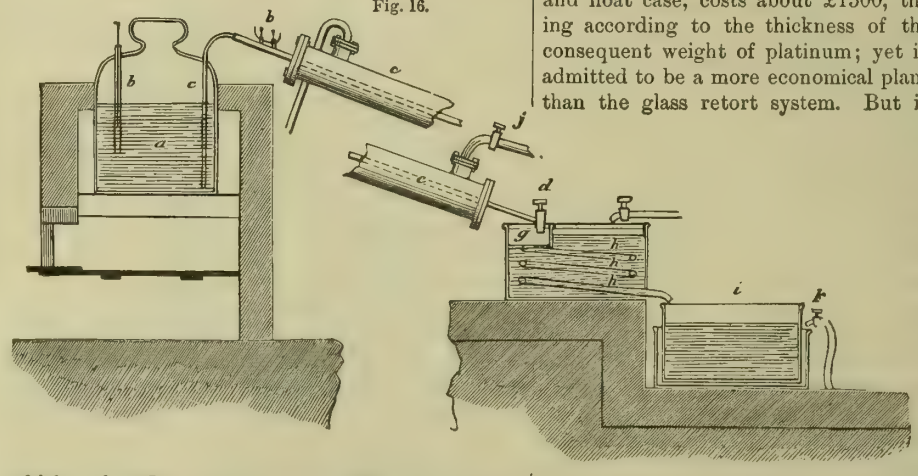


Fig. 16.



which a glass float is placed to indicate the depth of liquid in the still; c is a siphon, also of platinum, of the same diameter as the tube just mentioned. This siphon is inclosed in an iron tube, and between these two tubes a current of water can be passed. The siphon terminates in a platinum tap at d. The body of the still rests on a circular tile of refractory clay; the fire being below this tile, the flame rises at the back of the still, circulates round the sides, and finally passes from thence under the stock-pan. When sufficiently concentrated, if the running-off siphon, c, is not set, the workman proceeds to do this by closing the tap, d. The two plugs are removed in the funnel, and the siphon is filled with vitriol; the plugs are replaced. It now only remains to open the tap, when the contents of the still begin to run off. The tap is allowed to remain open, until from 3 to 4 inches of the still contents are drawn. The workman is guided in this by the indications of the glass float before spoken of, which serves as a gauge. The acid falls into the cup, g, thence it flows through the serpentine coil of pipe, h, h, h, which is immersed in water; and finally it emerges still slightly warm at the end of the coil, and runs into the receiving vessel, i, which vessel stands within another one, a stream of cold water from the tap, k, circulating between the two. The water tap, j, is also turned, when running off, so that a stream of cold water cools the siphon itself. When the operation is over, the workman proceeds to repeat the course of operations just described; be fills up his still to its former level, attends to his fire, heats it up to the proper point, and again allows the acid to run off.

Such an apparatus, the still itself having a capacity of from 70 to 80 gallons, is capable of producing thirty carboys of rectified oil of vitriol in twelve hours. A retort of the above dimensions, with the siphon and float case, costs about £1500, the price varying according to the thickness of the metal, and consequent weight of platinum; yet it is generally admitted to be a more economical plan of operating than the glass retort system. But it is not free from disadvantages; it is necessary to be careful that the vitriol contains no nitrous compound, for if this be the case, the platinum is rapidly attacked. To obviate this it is usual to add a quantity of sulphate of ammonia to the acid, while in the leaden concentrating pan, before it enters the still.

The strength of oil of vitriol is almost always determined by a reference to its spec. grav. Twaddell's hydrometer is that which is most commonly used.

The following table, by Dr. Ure, gives the amount of sulphuric acid and of sulphuric anhydride in oil of vitriol of different degrees of density:—

H_2SO_4.	Specific Gravity.	SO_3.	H_2SO_4.	Specific Gravity.	SO_3.
100	1·8485	81·54	50	1·3884	40·77
99	1·8475	80 72	49	1·3788	39·95
98	1·8460	79·90	48	1·3697	39·14
97	1·8439	79·09	47	1·3612	38·32
96	1·8410	78·28	46	1·3530	37·51
95	1·8376	77·46	45	1·3440	36·69
94	1·8336	76 65	44	1·3345	35·83
93	1·8290	75·83	43	1·3255	35 06
92	1·8233	75·02	42	1·3165	34 25
91	1·8179	74·02	41	1·3080	33·43
90	1·8115	73·39	40	1·2999	32 61
89	1·8043	72 57	39	1·2913	31·80
88	1 7962	71·75	38	1·2826	30·98
87	1·7870	70·94	37	1·2740	30·17
86	1·7774	70·12	36	1·2654	29·35
85	1·7673	69·31	35	1·2572	28·54
84	1·7570	68·49	34	1·2490	27·72
83	1·7465	67·68	33	1·2409	26·91
82	1·7360	66·86	32	1·2334	26·09
81	1·7245	66·05	31	1·2260	25 28
80	1·7120	65·23	30	1·2184	24·45
79	1·6993	64·42	29	1·2108	23·65
78	1·6870	63·60	28	1·2032	22·83
77	1·6750	62·78	27	1·1956	22·01
76	1·6630	61·97	26	1·1876	21·20
75	1·6520	61·15	25	1·1792	20·38
74	1·6415	60·34	24	1·1706	19·57
73	1·6321	59·52	23	1·1626	18·75
72	1·6204	58·71	22	1·1549	17·94
71	1·6090	57·89	21	1·1480	17·12
70	1·5975	57·08	20	1·1410	16·31
69	1·5868	56·26	19	1·1330	15·49
68	1·5760	55·45	18	1·1246	14·68
67	1·5648	54·63	17	1·1165	13·86
66	1·5503	53·82	16	1·1090	13·05
65	1·5390	53·00	15	1·1019	12·23
64	1·5280	52·18	14	1·0953	11·41
63	1·5170	51·37	13	1·0887	10·60
62	1·5066	50·55	12	1·0809	9·78
61	1·4960	49·74	11	1·0743	8·97
60	1·4860	48·92	10	1·0682	8·15
59	1·4760	48·11	9	1·0614	7·34
58	1·4660	47·29	8	1·0544	6·52
57	1·4560	46·48	7	1·0477	5·71
56	1·4460	45·66	6	1·04 5	4·89
55	1·4360	44·85	5	1·0336	4·08
54	1·4 65	44·03	4	1·0268	3·26
53	1·4170	43·22	3	1·0206	2·45
52	1·4073	42·40	2	1·0140	1·63
51	1·3977	41·58	1	1·0074	0·82

To bring the degrees of TWADDELL'S hydrometer to those of the real specific gravity, consider them as decimals, multiply by 0·5, and add 1·000; thus, supposing a sample of vitriol to stand 150° on TWADDELL'S hydrometer:—(·150 × ·5 + 1·000 = 1·750). Now, to ascertain the amount of real sulphuric acid in this sample, it is only necessary to run through the table and find the density 1·750°, or the nearest approach to it, which in this case is 1·746°. It will be found then that the sample would contain 83 per cent. of the monohydrated acid, or 67·68 per cent. of dry acid.

This method of arriving at the value of a sample, though very convenient, is liable to error. For instance, the sample might contain foreign matter dissolved in it; this would augment the density, and cause it to appear of more value than it really is. A slight change of temperature also will alter the density considerably. The following table, the production of PARKES, shows the gradual lowering of the density as the temperature increases, so that, even though the sample may be free from foreign bodies, error may creep in. From this table it is evident that the density of all samples of vitriol should be taken, as in the case of Dr. URE'S table, at as near as possible 60° Fahr.:—

PARKES' TABLE OF VARIATIONS IN DENSITY OF CONCENTRATED SULPHURIC ACID THROUGH CHANGE OF TEMPERATURE.

Temperature.	Density.	Temperature.	Density.
Degrees Fahr.		Degrees Fahr.	
30	1·8593	52	1·8511
32	1·8563	56	1·8500
36	1·8546	60	1·8468
38	1·8532	63	1·8449
40	1·8527	68	1·8435
42	1·8520	70	1·8430
44	1·8522	74	1·8413
46	1·8519	80	1·8381
48	1·8517	84	1·8343

Again, when the density of a sample is high, it is difficult to estimate it with sufficient accuracy. Thus on URE'S table, acid of 1·8439 specific gravity contains 97 per cent. of monohydrated acid, while the density of the monohydrated acid itself is but 1·8485—thus the slight difference of ·0046, or rather less than 1° on the hydrometer, equals 3 per cent. To obviate this, Dr. DALTON proposed that the boiling point should be taken as the guide, instead of the specific gravity, inasmuch as it permits a range of 10° or 12° for 1 per cent. of real acid. For this purpose he drew up the following table:—

DR. DALTON'S TABLE OF BOILING POINTS OF SULPHURIC ACID AT DIFFERENT STRENGTHS.

Specific Gravity.	Dry Acid Per Cent.	Boiling Point.	Specific Gravity.	Dry Acid Per Cent.	Boiling Point.
		Degrees.			Degrees.
1·850	81	620	1·769	67	422
1·849	80	605	1·757	66	410
1·848	79	590	1·744	65	400
1·847	78	575	1·730	64	391
1·845	77	560	1·715	63	382
1·842	76	545	1·699	62	374
1·838	75	530	1·684	61	367
1·833	74	515	1·670	60	360
1·827	73	501	1·650	58·6	350
1·819	72	487	1·520	50	290
1·810	71	473	1·408	40	260
1·801	70	460	1·300	30	240
1·791	69	447	1·200	20	224
1·780	68	435	1·100	10	218

In addition to these methods a very common mode of testing the value of vitriol is by an acidimetrical process, with a standard solution of alkali.

TARTARIC ACID.—*Dextro-tartaric Acid, Dextro-racemic Acid. Acid Tartrique*, French; *Tarter Säure, Tartryl Säure, Wein Säure, Weinstein Säure*, German ($C_4H_6O_6$).

Tartaric acid was isolated by SCHEELE in 1770. It exists largely in grape juice as acid-tartrate of potassium, and is widely diffused through the vegetable kingdom. In tamarinds, in the berry of the mountain ash, in madder, potatoes, cucumbers, quassia, squills, mulberries, pine apples, artichokes, sorrel girkins, black pepper, &c., it is found in the free state, or as a potassium or calcium salt.

Dextro-tartaric acid forms anhydrous, hemihedral, rhombic crystals, which turn the plane of polarization of a ray of light to the right.

A modification exists having the same formula, the same crystalline form, but inclined the opposite way, which turns the plane of polarization to the left; this is called Lævo-tartaric or Anti-tartaric acid.

Other forms of tartaric acid are:—Para-tartaric or Racemic acid ($C_4H_6O_6$), optically inactive, but capable of being separated into equal quantities of dextro and lævo tartaric acids:—Inactive tartaric acid or Meso-tartaric acid ($C_4H_6O_6$), optically inactive, and incapable of yielding dextro and lævo tartaric acid. Para-tartaric and Meso-tartaric acids form hydrated, holohedral, triclinic crystals.

Meta-tartaric acid ($C_4H_6O_6$) is produced by heating dextro-tartaric acid; it is deliquescent and uncrystallizable.

MANUFACTURE.—Dextro-tartaric, *i.e.*, ordinary tartaric acid, is prepared from acid tartrate of potassium (cream of tartar), on the large scale, from crude tartars.

Potassium tartrate is deposited from wine during vinous fermentation. Its solubility diminishes as the percentage of alcohol increases; hence the amount of argol or crust is to some extent a measure of the strength of the wine. In the Rhine provinces a considerable amount of argol is extracted from the skins and other solid portions of the grape.

The materials from which tartaric acid is made may be classed as "lees," "argol," and "tartar." Lees is the solid matter collected from the bottoms of the fermenting vessels. Argol is the thin crystalline crust deposited on the sides of these vessels. Tartar is manufactured from the two former by a rough process of extraction with hot water and crystallization.

Lees.—Italy is the great producer of the tartar manufactured in England; a smaller quantity comes from France. In countries where the wine is plastered the lees contain calcium tartrate instead of acid tartrate of potassium, and consequently there is little material from which tartar can be made. ROBERT WARINGTON gives the following analyses of lees received at J. B. LAWES' Citric and Tartaric Acid Works:—

	Tartaric Acid as		Total Tartaric Acid.
	Potassium Bitartrate.	Calcium Tartrate.	
Italian lees, 33 samples,.....	24·1	6·1	30·2
Greek lees, 14 "	19·9	11·8	31·7
French lees, 9 "	17·3	6·0	23·3
" 30 "	5·3	20·5	25·8
Yellow Spanish lees, 59 samples,	8·7	18·2	26·9
Red Spanish lees, 17 "	8·8	17·4	26·2

Argol exhibits a wide range of composition, containing from 40 to 70 per cent. of tartaric acid. Very low argols resemble superior lees, while first class argols are equal to ordinary tartar. In argol even of low quality the tartaric acid is chiefly present as potassium bitartrate.

Tartar, as already mentioned, is manufactured from lees or argol by extraction with hot water and crystallization. The highest quality tartars are those of South Italy and Messina; they contain about 76 per cent. of tartaric acid, and in some instances reach as much as 77 per cent. (pure potassium bitartrate would contain 79·7 per cent. of tartaric acid). Of this tartaric acid $1\frac{1}{2}$ to $3\frac{1}{2}$ is present as calcium tartrate. The tartars of St. Antimo or Naples contain 74 to 75 per cent. of tartaric acid of which 3 to $4\frac{1}{2}$ exists as calcium tartrate. Vinaccia tartar is made in various parts of Italy and France, from the solid matter of the grape remaining after the must is expressed. This solid matter is fermented, distilled, and tartar made from the residue; it contains 70 to 73 per cent. of tartaric acid, of which 5 to 7 per cent. are neutral tartrates. French tartars contain more calcium tartrate than good Italian tartars. (ROBERT WARINGTON, *Chem. Soc. Jour.*, vol. xxviii.).

Tartaric Acid.—In England, 2 tons of tartar are placed in a vat holding about 4000 gallons, and dissolved in about 2000 gallons of water; chalk or whiting is then added till effervescence ceases (100 parts of potassium acid tartrate, $C_4H_5KO_6$, requires 24 parts of chalk). The mixture is kept in motion by a steam jet, and by rotating arms, to prevent coagulation of the calcium tartrate. The reaction is:—

Potassium acid tartrate.	Calcium carbonate.	Potassium tartrate.	Calcium tartrate.			
$2\,C_4H_5KO_6$	+ $CaCO_3$	= $C_4H_4K_2O_6$	+ $C_4H_4CaO_6$	+ H_2O	+ CO_2	

The potassium tartrate is decomposed by boiling for two hours, with constant agitation with calcium sulphate from a previous operation, a slight excess being employed. The result is that the whole of the tartaric acid combines with the calcium, leaving potassium sulphate in solution.

The "generator," as the vat is termed, is allowed to cool, and the supernatant liquid run off and set aside to crystallize, the potassium sulphate being a valuable bye-product.

The calcium tartrate is well washed in cold water (it is slightly soluble in hot), and then decomposed by addition of sulphuric acid. The results are free tartaric acid and calcium sulphate. The amount of acid required is estimated from the weight of chalk used and the calcium contained in the tartrate of lime.

The mixture is next run into a tank having a perforated false bottom, lined with thick flannel, or into some other filtering apparatus. The sulphate of lime must be carefully washed to secure the whole of the tartaric acid.

The filtrate is evaporated in leaden pans, heated by steam coils or in the steam vacuum pan invented by EDMUND E. PONTIFEX. Tartaric acid is decomposed, especially in presence of sulphuric acid, at 150° Fahr. In the vacuum pan the temperature of the first solutions need not exceed 120° to 130° Fahr.

The first crop of crystals is highly coloured; it is therefore dissolved and heated with animal charcoal, and freed from phosphates by long boiling with hydrochloric acid.

Tartaric acid crystallizes in large transparent oblique prisms, having the specific gravity 1·739. It has an agreeable sour taste, is very soluble in water and alcohol, insoluble in ether; after long standing in the air its solution becomes covered with a fungus.

Tartaric acid melts at 170° to 180° C. (338° to 356° Fahr.), and is converted into metatartaric acid; on increasing the heat, water is given off, and tartralic (isotartaric or ditartaric acid) is formed—

$$\underset{\text{Tartaric acid.}}{2C_4H_6O_6} = \underset{\text{Tartralic acid.}}{C_8H_{10}O_{11}} + H_2O.$$

At a further stage tartrelic acid is formed thus:—

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} = \underset{\text{Tartrelic acid.}}{C_4H_4O_5} + H_2O.$$

Continuing to heat, ultimately tartaric anhydride isomeric with tartrelic acid is produced.

A further increase of heat decomposes tartaric acid into a variety of compounds, whose composition is dependent on the temperature and mode of heating. A sharp sudden heat causes evolution of acetic acid, carbonic acid, and carbonic oxide.

Tartaric acid is used by dyers and calico-printers, in medicine, and for the preparation of effervescent draughts. In the blood, tartrates are changed to carbonates. Tartaric acid is dibasic, its salts are tartrates.

Potassium Acid Tartrate.—*Bitartrate of Potash, Cream of Tartar, Argol.*—$C_4H_5KO_6$.—This salt is prepared from argol or lees of wine. The crude tartar is ground to powder, wetted with water, and thrown into vats heated to 212° Fahr. After two or three days the clear liquor is run off into earthenware pans to crystallize. The crystals are redissolved, 4 to 6 per cent. of clay and animal charcoal added, and the solution evaporated till a thin crust forms on the surface; it is then run into conical coolers. In a week or ten days the cream of tartar is found to have crystallized on the sides of the vessel, whilst the clay and charcoal, and most other impurities, have settled to the bottom. The crystals are dried on tiles, in the sunlight if possible, to improve their colour.

At Venice the acid tartrate of potassium is purified by repeated crystallizations; white of egg and wood ashes are added, causing effervescence and the upheaval of impurities, which are then skimmed off.

Cream of tartar crystallizes in hard, opaque, oblique rhombic prisms, of snowy whiteness when pure, and of sour taste; soluble in 180 parts of cold and 6 of boiling water. Its hot concentrated solution, if suddenly cooled, is covered with a layer of dense fine white crystals; hence the term "cream of tartar."

Potassium tartrate, $C_4H_4K_2O_6$, the neutral salt, is prepared by adding carbonate of potassium to the acid salt. The addition of most acids to a solution of this salt precipitates the acid tartrate. In alcohol it is nearly insoluble. Heated to redness in close vessels, a mixture of carbonate of potassium and charcoal results—much used as *black flux*. Calcined with its own weight of nitre, *white flux*, or carbonate of potassium, is obtained.

Rochelle Salt.—*Seignette Salt, Potassium and Sodium Tartrate*, $C_4H_4KNaO_6 + 4H_2O$.—This beautiful salt was discovered by Seignette at Rochelle. It is prepared by forming a concentrated solution of cream of tartar, neutralizing the acid with sodium carbonate, and evaporating till a skin forms on the surface; the liquor is then run into coolers and allowed to crystallize. The mother liquors, if concentrated, yield a second crop of crystals.

Rochelle salt forms large transparent right rhombic prisms, with hemihedral faces, which effloresce in the air. It dissolves in 3·3 parts of water at 3° C., 2·4 at 11° C., and 1·50 at 26° C. It is chiefly used in medicine.

Tartar Emetic.—*Potassio-antimonious Tartrate, Tartarus stibiatus. Brechweinstein, Speissglanzweinstein*, German. $C_4H_4K(SbO)O_6 + \frac{1}{2}H_2O$. The discovery of this salt was attributed to Mynsicht (1631), but it was mentioned by Basil Valentine two hundred years earlier, and was probably known long before that time.

It is prepared by boiling 3 parts of antimonious oxide with 4 parts potassium acid tartrate for about half an hour, filtering the hot solution, and crystallizing. The salt is purified by repeated solution and crystallization. The crystals form colourless, shining, rhombic octahedra; their taste is at first sweetish, then metallic. They are soluble in 14 parts of water at 15° C., in 2 parts at 100° C.

TIN.—*Etain*, French; *Zinn*, German; *Stannum*, Latin; Κασσίτερος, Greek. (*Jupiter* of the alchemists). Symbol, Sn. Atomic weight, 118. A malleable white metal, having a yellow tinge; when warm it possesses a peculiar odour. It is not readily oxidized by moist air. It possesses little tenacity, but can nevertheless be hammered out into thin sheets, barely $\frac{1}{1000}$ inch in thickness. This tin foil when amalgamated with mercury forms the "silvering" of mirrors. The specific gravity of tin is 7·29. Tin melts at 222° C.; 237° C. (Person.) It boils at a white heat, and burns in the air with a dazzling flame; at a red heat it decomposes steam, hydrogen being given off.

Tin is not soluble in concentrated, but is rapidly attacked by dilute nitric acid. Strong hot hydrochloric acid forms tin dichloride with evolution of hydrogen.

This metal is of high antiquity; it was employed by the Egyptians, is mentioned in the books of Moses, and has been known to the Chinese from time immemorial. From the writings of Dioscorides, Diodorus, Pliny, and others, as well as from Celtic records, it appears that a considerable trade with Cornwall and Devon for tin existed as long ago as 1040 B.C. The Phœnicians, the principal carriers of the metal, called it *stan*, whence the *stannum* of the Romans, and also the term *Stanneries*, which is still applied in Cornwall to the districts where the tin is produced.

The earliest direct evidence is that given by Herodotus, who, writing in the 4th century B.C., stated that tin was brought from the Cassiterides, under which name parts of Cornwall and Devon

were intended. R. N. WATTS (Royal Cornwall Polytechnic Society, 42nd Report) considers that inferential geological evidence carries back the commencement of tin-working to a time when the mammoth either still existed or had not long disappeared, and when the general level of Cornwall and Devon was at least some 30 feet higher than it is at present.

Previous to the thirteenth century England enjoyed a monopoly of the tin trade; but in that age rich veins of tin ore were discovered in Misnia and Bohemia, and about the year 1250 the English trade was much reduced by the low price at which the Germans were able to sell their tin. At present tin mines are wrought in Bohemia, Saxony, and Austria; in Galicia, on the borders of Portugal; at Piriac, in the Loire Inférieure; and at Vaulry, in the department of Haute Vienne in France; but the mines of French localities are of very little importance. Large quantities of tin ore occur in the Siberian mining district of Nertschinsk, and it is found in Dalecarlia in Sweden; but the richest deposits that have hitherto been found are those in the province of Tenasserim, on the east side of the Gulf of Martaban, in the Malayan peninsula; these have been worked for many centuries, and considerable quantities are still obtained. In the early part of the last century (1710) large quantities of very pure ore of tin were discovered in the island of Banca, whence as much as 3500 tons of the metal have some years been abstracted. Minerals of tin exist also in Brazil, in Mexico and Chili, in South America, in the United States, and very largely in Tasmania and Australia. The extent of tin-bearing country in New South Wales is about 8500 square miles. Of this area only about 8 square miles had up to 1877 been opened; the value of the tin raised amounted to £2,376,000.

The chief tin ore is cassiterite (tin stone, stream tin, &c.) SnO_2; it is found in veins and drift deposits accompanied by wolfram. In the alluvial deposits native gold is found with the tin.

The tin mining districts of Cornwall and Devonshire are three in number, viz.—1, that included in the south-west of Cornwall beyond Truro; 2, the neighbourhood of St. Austell; and 3, of Tavistock in Devonshire. The chief tin mines in these districts are Wheal Vor, near Helston; Polberrow, near St. Agnes; Polgooth, near St. Austell; Drake Walls, near Tavistock, on the Cornish side of the Tamar; and Birch Tor, also near Tavistock, but on the eastern side in Devonshire. Ores of tin are found in the form of regular lodes or veins disseminated in granite and in felspar—porphyry or elvan—and in alluvial formations, "stream tin," on the slopes of hills, or in the valleys. In the former instances the veins frequently cross one another, either horizontally or in their perpendicular descent; occasionally they ramify through the rock in all directions, producing at the point of intersection masses of ore called by the Germans *stockwerk*, such as the Altenberg mine in Saxony. In the other instance of the occurrence of tin ore, namely, in alluvial deposits, it is usually called *stream tin*, as well from the nature of the deposit, as from the fact that in these cases the workings are generally in the course of rivulets or streams. It is found either in a pulverized sandy state, in separate stones, called *shodes* in Cornwall, or in a continued course of stones, which are sometimes found together in large numbers.

It is probable that the deposits of stream tin were first discovered. Rivers swollen by the rain would cut deep gullies through the alluvium of their valleys, and expose the layers of tin stone, pebbles, and gravel; but as the searchers worked upwards they could not fail to discover some traces of the veins from which the stream tin had been derived, and regular mining would result. Hence, unquestionably, arose the practice of "shoding," the oldest method of search for mineral veins of which there is any record. Three centuries since both stream and lode works were thus sought after. R. CAREW, in his "Survey of Cornwall," 1602, describes the finding of tin stones "lying on the face of the ground, which they term 'Shoad,' as shed from the main 'Load,' and made somewhat smooth and round by the waters washing and wearing, . . . affordeth a tempting likelihood; the Tynners go to worke, casting up trenches before them in depth 5 or 6 foote, more or lesse, as the loose ground went, and 3 or 4 in breadth, gathering up such shoad as this turning of the earth doth offer to their sight."

This was the way to find stream tin. In searching for a "lode" a different plan was pursued. The shode lay open on the grass, or but slightly covered; guessing at the place where it had broken off, they sunk a shaft 5 to 6 feet long, 2 or 3 broad, and 7 or 8 deep. If they found the lode, well; if not, they tried again.

Similar in principle, though more methodical in practice, was the mode of search carried on a hundred years later. After any great land-flood the banks of the streams were carefully searched for shode stones; when found, the first step taken was to sink an assay "hatch" or shaft, 6 feet long and 4 feet broad, to the rock. If shode was found therein, the distance from the lode was estimated by the distance of the shode from the rock. More hatches were then sunk higher up the hill, not following each other, but alternately on either hand. When the lode was attained, that hatch was called a "tin hatch," and sinking was commenced.

"Costeaning" was an economical development of this process. Little pits were sunk from 6 to 12 feet deep, and drifts carried from one to the other across the direction of the veins.

The art of shoding and its allied operations has now almost died out, so far as Cornwall is concerned, since there are now few districts in that county in which the direction and nature of the lodes are not known; but in Australia and Tasmania, where the mines are as yet almost unknown, the old processes of exploitation might with profit be revived.

The stream works were the chief sources of tin supply down to late in the last century. At present streaming is all but extinct, though there are still

some stream works in out-of-the-way localities; and the refuse of the hatches, carried by the "red rivers" that run down to the sea in West Cornwall, is washed over and over again by successive operations to the water's edge.

Lodes were at first wrought in open workings, and this method has been followed almost continuously ever since the date of its adoption.

Carclaze, near St. Austell, is an open excavation of this kind, in which tin has been raised for centuries. Another work of the same character is now in full operation at Rock Hill, about four miles north of St. Austell.

"Shammeling," or "shambleing" is intermediate between open working and mining proper. The lode being found, the miner went down about 1 fathom, and there left a square platform called a "shamble;" he then descended again and continued thus from east to west, leaving shambles at each descent, until the lode grew too small or degenerated into mundic, maxy, &c. A drift was then made into the hill to follow the lode. Thus the shaft was divided into a series of step-like stages, each of such a height that a man could conveniently heave the stuff with a shovel from one to the next above.

Large stream works, as clay works often are now, were wrought in stages or steps; and shammeling was an adaptation of this method.

Shaft and level mining have, at the present day, superseded all other methods. Originally the lodes were followed from the shafts at points where they were rich, without any attention to order or regularity. Many of the early shafts were so narrow that they could be ascended and descended by climbing, like chimneys. "Stoping" downwards from the shaft was the next stage; then came the introduction of "winzes," and "stoping" downwards from the levels; finally, stoping upwards, as now practised. Both systems of stoping, the under and the over hand, were practised in Germany long previous to their introduction into this country. The advantages of overhand stoping caused it to be rapidly adopted, but the old method of working was continued in Wheal Alfred till 1816, and is occasionally followed even now.

Three hundred years ago 40 to 60 fathoms was the greatest depth attained; the lode was then followed as it lay, ventilating shafts being driven and the earth propped up by timber. In 1775 Dolcoath had been sunk 90 fathoms. Since then the extreme depth of Cornish mines has been nearly quadrupled, and continues to increase.

Dressing the Ore.—The order of treatment is much the same as that for copper ores. The clay and other light impurities are washed away by a stream of water; the stones containing the ore are then "spalled," *i.e.*, broken into small pieces by a stone-breaking machine, and the whole separated into heaps of different classes, according to the nature of the gangue. The richest lumps are called "best work."

The several heaps are further reduced by a stamping mill to a fine powder. The old stamp consists of a wooden shaft connected with a water wheel or steam engine, in which are arranged a number of cams, that catch the lifting arms of a series of pestles heavily shod with iron, and working in an iron-lined box. Four stampers, weighing 2½ to 3 cwts. each, are worked in each box, and each pestle is so lifted that the strokes follow in succession. A stream of water entering the box from above conveys the reduced ore, through gratings, over an inclined plane to a tank. Here the ore, in consequence of its gravity, arranges itself into three kinds; the heaviest, and therefore the richest, rests on the upper part of the inclined plane, a less rich ore in the middle, and the poorest or gangue parts are carried over into the tank or slime pit, where it settles to the bottom to be occasionally collected.

There are many different forms of stamps at present at work; amongst others may be mentioned ENNOR'S, in which power is economized by reduction of friction, and which, by means of a sloping stamp's grate, allows the stuff when broken sufficiently fine to escape at once. HUSBAND'S pneumatic stamper and WILLOUGHBY'S spring stamper are in use at several important mines. The CHATWOOD & STURGEON'S steam stamper is on the principle of the steam hammer; the steam not only raises the head, but impels it downwards. As the effect of the blow increases as the square of the velocity, an enormous battering power is added to the stamp by a moderate increase in its velocity.

The ram works in a closed cistern or coffer, entirely surrounding the ram head, and having a series of openings in which sieves or gratings are fitted, and through which the ore passes when sufficiently crushed. These are fixed a little above the level of the anvil face, in order to avoid liability to breakage; but the material is lifted to the height of the gratings by the action of the blow, and passes out with the stream of water which is kept continually flowing through. The ore is fed under the stamp, in just the quantity suitable for one blow. The ram weighs about 15 cwts., and will strike 150 blows per minute with a force of about 300 tons to each blow.

The HUSBAND'S stamp is thus described by R. GOLDSWORTHY. It consists of a piston working in a gun-metal cylinder, actuated by a crank driven by a belt and pulley from an engine. The piston and piston-rod are in one, with a chilled shoe attached. The cylinder is provided with holes above and below the piston, for egress and ingress of air. The air confined in the cylinder on the up stroke becomes compressed, and on the return stroke, like a spring, reacts on the piston, giving impetus and force to the blow. The piston rod is hollow, having a pipe inserted in the upper end, conveying a constant flow of water for the purpose of keeping the piston and cylinder cool, and supplying water to the coffer. The stuff is never operated on after it is once fine enough to go through the screen, which is extended the whole length of the coffer.

In the United States revolving stamps are much

used. The lifters work in guides in the ordinary way; but instead of the usual "tappets," or tongues, a round collar is fitted tightly on them. A separate cam is provided for each head. The cams are constructed in the form of an involute curve with an increasing radius, and act upon the side of the collar in close proximity to the lifter; the consequence is that the lifter and head are not only raised, but a rapid whirling motion is given to them which continues after release, so that the head both pounds and grinds the ore.

Rolls are also used for crushing. To produce good jigger work there should be a series; the upper set crushing the larger stuff may be fluted. They should be 30 inches diameter by 18 inches face, speed of periphery 50 feet per minute, provided with revolving screens or sizing "trommels," say, 72 inches by 24 diameter, and erected at an angle of 25° to that of the driving roller, working in water at a depth of 2 inches, which will effect a good separation and prevent balling of the earthy matter. By using sizing trommels only such portions are sent back as cannot be jigged. The ordinary "raff-wheel," or elevator, is used instead of the sizing trommels; it takes the stuff from the riddles and lifts it again to the hopper, so that nothing escapes which cannot pass through the riddle. If Blake's stone-crusher be used the flute rolls may be dispensed with. The best method of driving rolls is by strong spur gearing.

Before passing the stuff to the crusher it may be raked over a series of screens or riddles under a stream of water, which will result in a great saving of fine stuff, if caught by elevators or other suitable apparatus and carried direct to the sizing trommels. The great point to be observed is to granulate and not pulverize the stuff. The rolls should be set for different sizes and the stuff well screened between each crushing, in order that the fine may not be again subjected to pressure. The more fine or slime produced the more difficult to dress, and the greater the loss.

There appears to be some necessity for a machine to pulverize and grind the "roughs" or "tin rows," of which there are great accumulations at many of the Cornish mines. Dingey's is, perhaps, the most successful. This machine consists of a cast-iron circular dish, 6 feet in diameter, fitted with grate-plates around its sides, 15 inches by 5 inches. In this pan four cast-iron runners revolve, 2 feet in diameter, and weighing 1½ cwt. each, making 240 revolutions per minute, whilst the pan revolves slowly against the runners, changing their relative positions, and presenting a different surface of the pans to the shoes at each revolution. The ore is fed into the machine from the centre, and the stuff is carried down to the grinding surfaces through grooves cast in the discs. The power is derived from the engine by a belt, and the discs are worked by spur gear. The machine will grind 10 tons of roughs in ten hours, consuming 1½ cwt. of coal per ton of stuff produced.

Carr's disintegrator consists of four cylindrical iron cages, arranged within each other, and revolving on two shafts, one solid and the other hollow. The first and third cages are caused to rotate to the right, and the second and fourth to the left, with great rapidity, by means of an open and cross belt. The machine is fed from the centre, and the stuff is thrown by centrifugal force from the first to the second cage, which is revolving in a contrary direction; from thence to the third, and so on; until fine enough to pass through, when it flies off as powder from the outer cage. The cages travel at different velocities, from 40 to 60 feet per second, and so keep up a rapid and continuous agitation, striking an incalculable number of blows per minute. The machine will disintegrate 50 to 100 tons per day, according to the nature of the ore.

A self-acting ore-dressing machine, by G. Green, of Aberystwith, lately received the first silver medal of the Cornwall Polytechnic Society. It consists of a crushing mill, with rollers about 28 inches diameter by about 16 inches wide, into which the stuff is put after being "spalled" or broken down by the stone-breaker. This mill is above the dressing machines, so that the crushed and classified ore-stuff may be carried partly by gravitation, but principally by the force of the water current, into each of the machines provided for its separate treatment, according to the grade of its classification.

The classifier is a revolving sieve, or riddle, made in the form of a cylinder; it contains within it a perforated pipe, corresponding in length with the extent of the perforated surface, from which a spray of water is made to play upon the ore stuff. This washes through the sides of the classifier all the "slimes" and particles which are finer than the holes.

The size of the perforations is determined by the nature of the stuff. The richer it is in mineral the larger the holes, and *vice versâ*. The ore stuff which remains in the classifier is returned to the rollers, to be further crushed, while all that passes through the holes is delivered into a trough which conveys it to a slime cone. The dead slimes are here extracted from the coarser portions of the crushed stuff. All the stuff which passes through is washed by the water into a second classifier, whilst the extracted slimes overflowing at the top are conveyed by a separate "launder," or duct, to another series of classifiers.

The classifiers are so arranged that each one turns out a finer stuff than that above it. More or fewer are used, according to the nature of the stuff to be treated, and the quantity to be worked in a given time. The sized product is discharged at the end of each classifier into iron shoots, which convey it to a jigging machine to suit.

The jiggers are horizontal hutches, made of wood or iron, and divided into two, three, four, or more compartments, by transverse partitions. A vertical partition extends along the upper part of the compartments, having on one side of it a set of plungers to produce the jigging motion, whilst the series of sieves are placed on the other side, each at a slightly lower level than the one above it. The separation

of the materials in the jigger is effected by the motion of the water with which the hutch is filled, and which is made to work up and down through the sieves on the other side of the jiggers by the plungers. A layer of ore is deposited in the sieves, which has the effect of allowing particles of the same specific gravity to pass through it and the sieves, while it keeps back any particles of less specific gravity, which last are gradually washed over the end from one compartment to another, the light waste from the last compartment finally passing away.

The granular heterogeneous composition separated by the jiggers, and known as "raggings," is subjected to a series of stamps, and the pulverized material returned to one of the riddles.

Buddles, or other efficient slime machines, are attached to the larger classifiers, and the stuff flowing in a perfectly even current from the bottom of each classifier on to each separate buddle makes them quite self-acting, and very effective. All the labour required is to raise the deposited ore out of the jigger receiving box, and off the beds of buddles, to make room for other deposits. The finest, or "dead" slimes, are worked by an ordinary paddle trunk, or other slime washer.

The whole apparatus is complete and continuous, each distinct sized product having an apparatus suited in speed and action for its treatment, which is so situated that the materials treated are conveyed through from stage to stage by streams of water, and with the least possible manual labour.

Three propositions have to be observed in ore dressing. 1. The separation of minerals cannot be secured by gravity alone, owing to the irregular cleavage or fracture of the stone. If flaky, a greater surface will be exposed to the water; and this will to some extent overcome its specific gravity, and the particle will not find its proper place in the settlement.

2. Ores must not be reduced to too great fineness, or the heavier material will be separated with great difficulty. The stone should not be stamped lower than is requisite to separate the ore from its matrix. To effect this the first grates should be large enough to pass the granular ore, and finer ones should be used for the roughs.

3. The best machinery is that which reduces to a proper size, and classifies by trommels having a mesh suitable to the kind of ore under treatment.

The above principles may be carried out by the use of the machinery already described; but the ore-dresser must be a man of practical experience, having a knowledge of most machines and the kind of ore they are best suited for, since it is in this department that the mine is either made to pay or the reverse.

Trommels are for collecting the stuff together in various sizes, after which it is separated by one or other of the many ore-separating machines, such as jigs, buddles, cases, and trunks, sleeping tables, round tables, shaking tables, &c. Good classification is essential, but if carried too far (as on the Continent it sometimes is), it may entail a loss in working.

The clearing trommel deprives the vein stuff of earthy or clayey matter. Separating trommels divide coarse and fine-grained stuff for sizing trommels, which latter prepare stuff for jiggers and buddles.

The trommel may be either one long steel, iron, or zinc, conical perforated tube, divided into sections, or it may consist of a series of tubes. In either case, the tube sections or tubes are provided with meshes of different sizes, suitable to the class of stuff under treatment, and worked by one continuous shaft—all being so arranged as to be self-acting in every particular, so as to lessen labour on the dressing floor.

The washing trommels are about 4 feet in diameter by 9 feet long, fixed at an angle of 1° per foot. They make fourteen revolutions per minute, using 25 gallons of water per minute, and will deal with about 60 tons of stuff in a day of ten hours.

Jigging.—A machine very generally used is Petherick's Plunger Jig, with the Kley slide motion. It consists of a plunger worked in a cistern of water by a beam attached to a shafting supplied with spun gear. When the plunger is forced down the water in the cistern rises through copper sieves, perforated with holes suitable to the stuff under treatment, usually about $\frac{1}{16}$th of an inch diameter. By this means the stuff which has been laid on the sieves is kept in suspension, the lighter is forced to the top, and the heavier sinks to the bottom. The plunger works sixty strokes per minute for about ten minutes, is then allowed to rest for a moment; the top stuff is skimmed off and thrown aside, the bottom layer or ore is collected, and the operation repeated. A portion of the top stuff may, in some cases, be reworked.

Hunt's ore separator works on the same principle; it will treat 40 tons of low quality ore in ten hours, and uses very little water. The ore is supplied to the hopper with the water, which carries it into a copper sieve, perforated with conical holes about one-sixteenth of an inch on the under side, and very fine on the top. A plunger forces a steady flow of water through the sieve, and keeps the stuff in suspension. The sieve is sloping and provided with low partitions; in these the ores of different specific gravity settle, according to their respective specific gravities. Even precious stones, which are frequently found in alluvial gold, are saved by the delicate action of this machine. It has been extensively used for washing waste heaps.

Air jigs have been devised, which are employed where water is scarce; there are also other devices for separation, such as causing the ores to fall through a column of water; there are also settling tubs, sorting boxes, slime separators, shaking frames or tables, &c.

Buddles.—Many forms are in use: Borlase's may be taken as an example of the *concave*, or slime buddle. The ore is received on a central revolving pan, from which it is carried through pipes to the

circumference, and equally and regularly distributed from the outside to the centre. The buddle is 17 feet diameter, 14 inches deep, with an incline of $1\frac{1}{2}$ inch in 1 foot; a pipe $1\frac{1}{2}$ inch diameter conveys clean water. RITTINGER'S buddle is an obtuse wooden funnel, 16 feet in diameter. The surface is divided by strips of wood, three-fourths of an inch high, into thirty-two segments, each of which is terminated by a square iron shoot, through which the substance is washed and passed to parallel ring launders below. Eleven distributors are fixed above it, and discharge their contents at the periphery of the funnel. The ores are passed into a box and puddled by a rotating paddle. Other buddles are ZENNER'S, RULE'S, WILLIAMS', BOYN'S, HUET & GEYLER'S, &c.

The *convex*, or outward flow, is the ordinary round Cornish buddle; it is still used in most English mines. It is built about 24 feet in diameter, and usually has a 7 feet run from cone to circumference. The incline must be adapted to the ore to be treated. The cone, or distributor, is about 10 feet in diameter, and much more acute. This buddle requires a $1\frac{1}{2}$ inch pipe to supply it with water; brushes are connected to the pipes attached to the cone pan, and make three or four revolutions per minute. The ore having the greatest specific gravity settles nearest the distributor. This buddle is better understood, more easy of construction, lighter, and less expensive than most others.

It is to be remarked that in all dressing operations the cost of production is greatly increased by the huge quantity of water employed. R. GOLDSWORTHY. *Cornwall Polytech. Journal*, 41st Report.

The ore is now devoid of most of its earthy constituents, and is ready for smelting, except when associated with copper and iron pyrites, arsenic, &c., in which case roasting is resorted to. The mode of treatment has been already described, and the calciners figured under ARSENIC and COPPER, which see.

In some districts the ores are moistened with hydrochloric acid and sulphuric acid, or a mixture of both, to assist in removing the copper and iron; but they must not be covered with acid, as the air plays a considerable part in the oxidation.

Smelting.—The ores are assayed by fusion with powdered charcoal and ground borax glass, casting in an ingot mould. When cold the button of tin is detached and weighed. The flux may be equal parts of borax glass and sodium carbonate, or three parts sodium carbonate and one of lime. When the ores are very poor the wet assay is preferable.

The furnace commonly employed is shown in Figs. 1 and 2. Sometimes two casting pots are added. A, grate; B, fire door; C, bed; D, arch, having an air passage through it to prevent over heating; E, bridge; F, draught-hole, opened whilst skimming slags; G, working door; H, charging door; I, flue; K, casting pot; L, casting gutter closed by a clay plug.

The ore is mixed with 12 to 18 per cent. of anthracite coal in powder "culm;" a small quantity of lime or fluor spar is also added if it contains much silica; 20 to 25 cwts. of this mixture con-

Fig. 1.

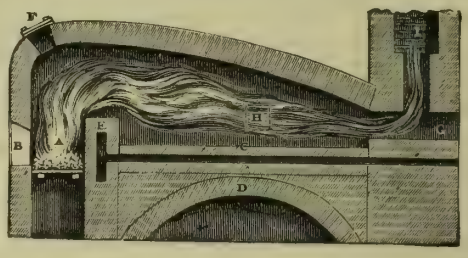
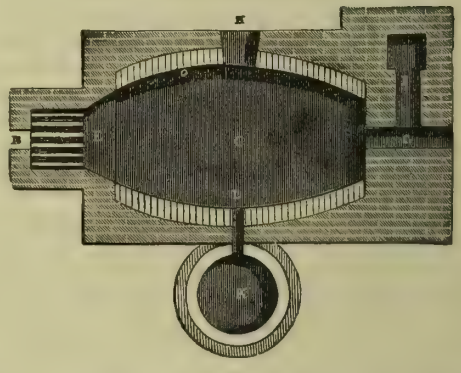


Fig. 2.



stitute a charge, which is spread on the furnace bed, the doors closed, and the fire gradually raised to its highest intensity. In six or eight hours the door, G, is opened, and the charge well rabbled and mixed. The doors are again closed to permit the furnace to recover its temperature. After a short time some moist slack is thrown on the surface of the fused mass, the draught-hole, F, opened to allow of the inspection of the furnace, and the scoriæ and slag carefully skimmed off. The last skimmings are sent to be restamped, since they contain about 5 per cent of metal. The first are thrown away.

When the bath is clean the plug at L is removed, and the tin flows into the cast-iron pot, K, where it remains long enough to allow the slag and impurities to rise to the surface and be skimmed off—the furnace being in the meantime recharged. The tin is finally cast in ingots of about 3 cwts. each in iron moulds, in each of which a piece of wood is fixed to form a hole in the ingot by which to hook it out when cold.

Small blast furnaces were formerly used; but the loss of metal and the consumption of fuel were found to be so large in comparison with that of the reverberatory furnace, that they have long been abandoned in England.

Tin is sent to market as "block tin," cast, as already described, in strips 2 feet long, 1 inch wide, and half an inch thick; and in the form of "grain tin," the last being produced by heating block tin to near the melting point, and dropping it upon a

hard substance, or striking it with a heavy hammer. The tin is, by either method, broken up into long crystalline fibrous columns.

Refining.—Blocks of tin are loosely piled in a reverberatory furnace, and a moderate heat applied; the pure tin melts and flows into the receiver, leaving in the furnace an alloy containing the more refractory metals. As the process goes on fresh blocks of tin are supplied, until 5 or 6 tons have run off.

The tin in the casting pot is then "boiled," or "tossed." "Boiling."—Billets of green wood are suspended over the casting pot by a crane, and forced down into the molten metal. Part of the tin is oxidised by the steam generated, but reacts on the particles of the more oxidisable alloyed metals, and eliminates them as oxide, being itself reconverted into the metallic state.

The scum which forms on the top is remelted with the next charge.

"Tossing" consists in taking up the metal in ladles and allowing it to fall back through the air into the casting pot, the oxidised matters being removed as formed.

After subsidence the metal is carefully dipped off, the top layer being set aside as the best metal for grain tin, the middle cast into moulds for common tin, and the bottom returned to the furnace for further purification.

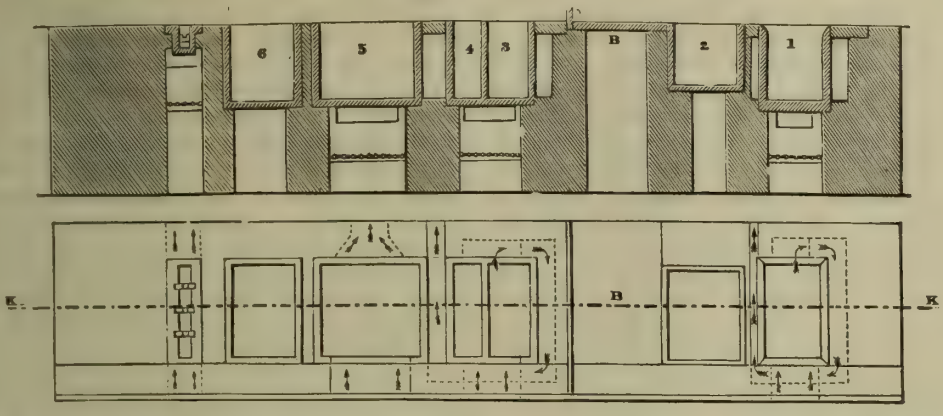
The principal uses of tin are for the manufacture of various alloys which are used in the arts, such as bronze, bell metal, solder, &c., and for making tin plates—*i.e*, sheet iron, coated with tin.

Tinfoil is made by passing slabs of tin backwards and forwards under a pair of rollers, the temperature of the metal being kept as nearly as may be 212° Fahr.

Tin Plates or Sheet Tin.—Iron, when perfectly clean, forms an alloy with molten tin, which enables it to be coated with the latter metal. As tin oxidises very slowly, it forms a beautiful and enduring coating to the more perishable metal.

The iron plates are prepared with very great care

Fig. 3.



from the purest metal. When required for tinning they are immersed in a bath of warm dilute oil of vitriol during fifteen or twenty minutes, are next rubbed with sand and water, and afterwards washed, when they are ready for annealing, which is conducted thus:—The plates to the number of about eighteen hundred—for common sizes—are placed in piles, within a cast-iron box about 2 feet square, the lid carefully luted on to prevent air entering, and then placed with several similarly filled ones in a stove constructed very much in the shape of a reverberatory furnace, but considerably larger, and having its bed on a level with the ground. The fire-bridge being tolerably high, the flame from the grate rolls slowly over the boxes, and raises them gradually to a cherry-red heat, at which temperature they are maintained during twelve hours, and then withdrawn. After being subjected to this process, the plates have a deep plum-colour bloom on their surfaces, due to a very thin film of ferric oxide upon them. They are now passed three times through a pair of hard, smooth, and brilliantly polished rolls placed in close proximity, so that the plates passing between them are subjected to a very great pressure, but not sufficient to enlarge them. After having been thus *cold rolled*, as it is termed, the plates possess a lustrous and dappled appearance. They are again annealed, but the heat is milder, and the time reduced to five or six hours. They are again immersed in a warm but more dilute bath of oil of vitriol than that already used, during ten minutes, then removed and well rubbed with sand and water, to detach all dirt and scale. They should now have a smooth, perfectly clean, greyish metallic surface, in which state they can be kept in cold water without injury for some time, and are ready for the tinning.

The apparatus or "stow"—Fig. 3—for this process consists of a series of baths set side by side, each bath having a fire beneath it, to keep the materials they severally contain in a fluid state. These baths or pots are six in number—namely, 1, the tinman's pot; 2, the tin pot; 3, the washing or dipping pot; 4, the grease pot; 5, the cold pot; and 6, the list pot. The tinman's pot is full of melted grease, and into this the plates are immersed and left till all moisture upon them is evaporated, and they become completely covered with the grease.

It is about 2 feet long, 15 inches wide, and 20 inches deep. They are next plunged into a bath of melted tin, protected with a layer of grease, and remain in it for about twenty minutes. This pot has a capacity of 22 × 18 × 16 inches. In the first dipping the alloy is imperfect, and the surface not uniformly coated; consequently the plates are removed to the dipping or wash pot, which is divided into two compartments. The first immersion takes place in the larger division, which contains molten tin covered with grease like the last, and here the plate is left sufficiently long to make the alloy complete, and to separate any superfluous tin which may have adhered to the surface. Each plate is then taken separately to a table, and is wiped on each side with a brush of hemp to remove any excess of tin; to obliterate the marks of the brush, it is dipped quickly into the second compartment of the wash pot, and then at once into the grease pot. This second compartment of the wash pot always contains the purest tin; and as it becomes alloyed with iron, it is removed to the first compartment of the same, and thence to the tin pot. The grease pot is filled with melted grease; and great care is necessary to maintain it at the proper temperature. Its purposes are to allow any superfluous tin to run off, and especially to prevent the alloy on the surface of the plate cooling more rapidly than the iron. If this were neglected, its surface would be cracked. After ten minutes' immersion in the grease pot the plate is removed to the cold pot, which is filled with tallow heated to a comparatively low temperature. The pots 4 and 5 serve the purpose of annealing the plates, and of cooling them down to a low temperature. The last one in the series is the list pot, and is a small cast-iron bath kept at a sufficiently high temperature, its bottom covered with tin to the depth of a quarter of an inch. The edges of the plates are dipped in this layer and left till the wire of tin, which usually forms on them in the course of the foregoing processes, can be removed by a quick blow on the plate with a stick.

The plates are now carefully rubbed, first, with bran to clean them from grease and dirt; and secondly, with a pad of sheep-skin, retaining its wool. They are then sorted according to their quality, and packed in boxes.

ULTRAMARINE.—See PIGMENTS.

VARNISH.—*Vernis*, French; *Firniss*, German—a fluid which when spread in a thin layer becomes by evaporation or chemical change a lustrous film impervious to air and moisture.

Nearly all varnishes are made by the solution of resins or gums, or combinations of these with oils, in some volatile substance. Their appearance and durability depend on the quality of the gums, and the nature of the solvents used.

The solvents commonly used are—alcohol, methylated alcohol, wood spirit, ether, naphtha, benzine, turpentine, bisulphide of carbon, essential oils, linseed oil, and its congeners.

The solids giving "body" are copal, shellac, dammar, sandarach, elemi, mastic, benzoin, rosin, asphalt, &c.

The colouring matters sometimes added are aloes, annotto, cochineal, dragon's blood, gamboge, indigo, saffron, turmeric, &c.

Spirit varnishes are made by dissolving gums and resins in a perfectly volatile medium, such as alcohol, turpentine, benzine, ether, and like fluids; they dry by evaporation of the solvent, and leave the gum upon the body varnished in a hard, lustrous coating, which is, however, apt to crack and peel off.

Oil varnishes are mixtures of drying oils with gums and resins subsequently dissolved in a spirit. They dry slowly in two stages. The evaporation of the spirit leaves a thin sticky film of the mixture of gum and drying oil, which in turn becomes by oxidation of the oil a firm, slightly elastic, continuous coating of the article varnished. The elasticity of the varnish when dry depends on the amount of oil which it contains.

The chief gums employed in the manufacture of varnish are described below.

Amber gives the most durable varnish known; it is, however, a very costly gum and hard to dissolve, so that its use is very limited. Amber is a hard, transparent or opaque, moderately tough body, with a smooth glassy surface. Its specific gravity is 1·06 to 1·07; hardness, 2 to 2·5; insoluble in water or alcohol and oils without decomposition. Alcohol extracts succinic acid and resin and a volatile oil from pounded amber, when treated with ether. In fact amber is a mixture of at least two resins. In order to prepare varnish from it, it must be fused for some time, and heated oil gradually added.

Various processes have been tried for making varnish from amber without loss of gum; the plans described below have of late years been revived.

"Powdered amber, with twice its weight of olive oil, was put into a wide-mouthed glass vessel; and a digestor or strong copper vessel being filled about one-third with water, the glass was placed in it, the cover of the digestor screwed down tight, and a moderate fire continued for an hour or more; when cold, the amber was found dissolved into a gelatinous mass."—(HOFFMAN, *Obs. Phys. Chem.*, 1736.)

STOCKAR in 1760 published an account of experiments made by ZIEGLER and himself. In this he states that "by continuing a simmering heat twelve hours, and confining the vapour as much as stoneware vessels would bear without bursting (the danger of which was avoided by making a small notch in the cork stoppers), powdered amber dissolved perfectly in expressed oils, in turpentine, and in balsam of copaiba: a strong copper vessel, with a cover screwed on it seems most eligible; and for greater security, a valve may be made in the cover, kept down by a spring." Moreover, by digestion for a week, in close-stopped glass vessels in which the compression could not be very great, solutions equally perfect were obtained.

The solution in rape-seed oil, and in oil of almonds, was of a fine yellowish colour; in linseed oil, gold-coloured; in oil of poppy seeds, yellowish red; in olive oil, red; in nut oil a deeper red.

The solution with turpentine was of a deep red

colour, and on cooling, hardened by evaporation of the spirit into a brittle mass of the same colour.

All the solutions mingled perfectly with spirit of turpentine. Those made with the oils of linseed, bays, poppy seed, and nuts, when diluted with four times their quantity of turpentine spirit, formed hard, tenacious, glossy varnishes, which dried quickly, and appeared greatly preferable to those made in the common way from melted amber.

Animé is imported from Brazil and the West Indies. It is the produce of the *Hymenæas courbaril*. It is a trsnsparent pale yellow gum. Brown American animé is employed for manufacturing gold size or japan black. Although superior to amber in its capacity for drying, and equal in hardness, varnish made from animé deepens in colour on exposure to air, and is very liable to crack. It is, however, much used for mixing with copal varnish.

Benzoin is a gum-resin but little used in varnishes on account of its costliness. The finer sorts are brittle, pulverulent, with conchoidal fracture; they fuse at a gentle heat.

Colophony is synonymous with rosin. When the resinous juice of *Pinus sylvestris* and other varieties is distilled, colophony remains in the retort. Its dark colour is due to the action of the fire. Dissolved in linseed oil or in turpentine by the aid of heat, colophony forms a brilliant, hard, but brittle varnish, which is apt to soften at temperatures above 80° Fahr. and become sticky.

Copal consists of several minor resins of different degrees of solubility. In durability it is only second to amber; when made into varnish, the better sorts become lighter in colour by exposure to air.

Copal is generally imported in large lumps about the size of potatoes. The clearest and palest are selected for what is called *body gum;* the second best forms *carriage gum;* whilst the residue, freed from the many impurities with which it is associated, constitutes the *worst quality*, fitted only for japan black or gold size.

Copal is tasteless and inodorous, transparent and of conchoidal fracture. Heat softens it without rendering it viscid. In alcohol it is but little soluble; but it is said to become more so by reducing it to a fine powder, and exposing it to atmospheric influences for twelve months. Boiling alcohol or spirits of turpentine, when poured upon *fused* copal, accomplishes its complete solution, provided the solvent be not added in too large proportions at a time. The addition of camphor also promotes the solubility of copal; so likewise does oil of rosemary.

The best African gum copal is a semi-fossil, found at a depth of 3 to 5 feet below the surface. It has been ejected from the trees at some indefinite distance of time. The gum from existing trees is of very inferior quality.

The copal trees, *Hymenæa verrucosa*, *Borrie*, are found in large numbers on the east coast of Africa, and cover extensive tracts of country to the eastward of the Waslungi range of mountains, from the Marni hills to the southern extremity of the range near Kilwee; lat. 6° S. to 9° S., long. 39° E. to 39° 46′ E. This district is not the only, but is at present the principal one, where copal digging is practised.

Of recent copals three varieties are used in making varnish, the hard, the semi-hard, and the soft. The two first are employed only in making oil varnish; the latter, with less resisting power, is used for spirit varnish.

The East Indian copal is produced from the *Elæocarpus copalifer*. American copal is the produce of the *Rhus copallina*.

In making varnish it is essential that the gums should be identical. H. Violette distinguishes the qualities by heating the copal in a steam jacket. Some fragments soften more or less; these are removed and considered "soft copal." The remainder of the gum is cast into a bath of melted tin, at about 300° C. Semi-hard copal melts and spreads, whilst hard copal resists and is only fused at a much higher temperature.

The solvents of hard and semi-hard copals are not known at present; that they exist is to be inferred from the fact that the resins flow naturally from the tree which produces them, in the form of a limpid liquid, which thickens and hardens by exposure to the air, losing by evaporation the solvent essential oil.

Up to the present time chemists have found no other way of dissolving hard and semi-hard copals in the mixture of oil of turpentine and oil, which is the vehicle used in making varnish, than by previously decomposing them by heat. The extent of this alteration effected by heat is of great importance, for the higher the temperature employed the deeper is the colour of the varnish, which in the operation loses its limpidity.

According to Violette the fusing and distilling temperatures of copals are :—

	Fusion.		Distillation.
Hard copal,.....	340° C.	....	360° C.
Semi-hard copal,.....	180° C.	....	230° C.

The above copals, when melted only, dissolve neither by heat nor cold in oil of turpentine. Their solution when effected corresponds, or is relative to, a certain degree of decomposition of the copal.

Violette, who made an exhaustive research on the subject, found that hard and semi-hard copals became soluble in a mixture of turpentine and linseed oil, only after losing 20 to 25 per cent. of their weight. Beyond a loss of 25 per cent. they became more and more soluble, but at the same time darker, and yielded less varnish, owing to the increased loss. To obtain the largest quantity of the best varnish the copal must therefore be distilled at about 360° C., until it has lost 25 per cent. of its weight.

Copal which has lost only 10 per cent. by distillation is soluble in turpentine, which has been thickened by prolonged exposure to air and light. Were it possible to procure this singular modification of turpentine by a short, easy, and cheap process, a great improvement might be made in the manufacture of varnishes.

The distillate "copal oil" is a limpid yellowish

liquid. Its density is about 0·80; it burns in the air, giving a bright light; it is soluble in oil and spirit of turpentine. It dissolves soft and semi-hard copals. It may usefully be employed in making varnish.

Makers in England habitually return the distillate to the gum pot before adding the hot linseed oil. This is done by fitting a cover to the gum pot in the shape of an inverted cone; the copal oil which is given off condenses and runs back upon the gum.

Acetone rendered anhydrous by rectification over chloride of calcium readily dissolves cold copal which has been previously heated to the point of fusion. One part of copal is soluble in 2·8 parts of acetone, producing a varnish which dries almost instantaneously when spread in a thin film, leaving a hard brilliant coating. A more concentrated solution is obtained, without separation of copal, by expelling part of the acetone by distillation. Evaporated to dryness, the remaining copal is more soluble in acetone than when in its original state.

The solubility of shellac in acetone varies according to the species of the lac. One part of artificially bleached shellac requires only 1·5 parts of acetone to form a thick solution like syrup. Some samples of coloured shellac are almost insoluble, whilst others dissolve in 3·5 parts of acetone.

Acetone dissolves with ease and in considerable quantities mastic and sandarach; dammar, yellow amber, and caoutchouc are, on the contrary, almost insoluble. The solution of acetone and mastic produces a very beautiful and brilliant varnish.

Lac constitutes the basis of spirit-varnish. The resin is soluble in strong alcohol aided by heat. Its solution in ammonia may also be used as a varnish, when the articles coated with it are not exposed more than an hour or two at a time to water.

Mastic is a soft resin of considerable lustre. The two sorts in commerce are, *in tears* and the *common mastic;* the former is the purer of the two. It consists of two resins, one of which is soluble in dilute alcohol. With oil of turpentine it forms a very pale varnish of great lustre, which flows readily and works easily. Moreover, it can be readily removed by friction with the hand; hence its use for delicate work of every description.

Sandarach is a pale odorous resin, less hard than lac, with which it is often associated as a spirit-varnish. It consists of three resins, differing as to solubility in alcohol, ether, and turpentine. It forms a good pale varnish for light-coloured woods; when required to be polished, Venice turpentine is added to give it body.

Dammar is a tasteless, inodorous, whitish resin, easily soluble in oils. It is not so hard as mastic, with which it forms a good admixture. Its solution in turpentine gives a beautiful lustrous pale varnish, which, however, after a few weeks is covered with a fine impalpable powder from disintegration of the gum.

Of the solvents of these various resins little need be said. In the manufacture of varnishes great care, as well as cleanliness, are required. The resins should be washed in hot water, to free them from particles of dust and dirt; they should be dried and assorted according to their colour, reserving the lightest shades for the best kinds of varnish.

Manufacture.—The English mode of making oil varnish is very simple, but requires great skill on the part of the workman. The gums are for the most part insoluble in oil until they have been heated for a length of time, which varies with the quality and nature of the gum; again, the temperature of the oil must correspond very nearly with that of the fused gum, or the two will not mix. These details of manipulation are very jealously guarded.

The varnish house ought to be quite detached from any other building. An occasional fire is one of the incidents natural to the manufacture, but by watchfulness and adoption of efficient means of extinction the loss is usually only that of a few gallons of oil or varnish.

The gum is melted in a copper vessel 2 feet 9 inches high, and 9½ inches across the bottom outside. The bottom is hammered out of a solid block of copper, in shape resembling a hat without a brim. The upper part of the pot is made of sheet copper, of a cylindrical form, 10 inches in diameter at the top and 2 feet 2 inches high, about three-eighths of an inch thick. The lower part of the cylinder is then rivetted to the bottom with copper rivets, the heads of which are inside. Previous to rivetting on the bottom, a flange of copper, of about three-eighths of an inch in thickness, is fixed horizontally round the pot on to the bottom part under the rivets. Near the top of the pot are two loop handles, on opposite sides, for lifting it on and off the fire.

The gum pot furnace is so far sunk into the ground that its covering plate is on a level with the pavement of the varnish house. The gum pot fits into a circular hole above the fire, resting on its flanges.

To prepare the gums for fusion they are reduced to pieces of about the size of a filbert, by cutting blows of a hammer, the gum being held on a lead anvil 2 inches thick and 8 inches square.

The oil is heated in a copper pot, fashioned in the same way as the gum pot. The diameter across the bottom outside is 20 inches: height of bottom, 7 inches; the cylindrical body of the pot is 2 feet 10 inches in depth, and joined to the bottom part with strong copper rivets. The handles are fixed to opposite sides, 7 inches below the rim, and should project at least 4 inches from the pot sides.

The furnace is built in a similar manner to that for the gum pot; the pot must not fit too closely to the circular hole, or there may be difficulty in lifting it off the fire. Alongside the furnace should be a low trolly on rails, so that the pot, if its contents should catch fire, may be rapidly conveyed into the open air, where it can be extinguished at leisure. Only those who have witnessed it can conceive the height of flame from even a small quantity of oil when strongly heated before ignition. The writer saw the flame from 1 pint of heated oil lick the rafters of a roof 15 feet above it.

The sizes given are those in ordinary use. In great factories the boiling pot is frequently much larger.

Previous to beginning to make varnish, the shed should be cleared of every unnecessary article. The vessels and stirrers must be perfectly clean. At a convenient distance from the furnace (outside, if the weather is fine) a bed is made 1½ inch deep of fine sifted ashes, to rest the boiling pot on when lifted off the fire: and about 4 feet from the ash bed is placed an iron plate with a circular hole to receive the gum pot.

A typical process is conducted as follows:—The boiling pot is set on the fire with 8 gallons of clarified oil (linseed oil, boiled with or without driers); then the gum pot is put on with 8 lbs. of gum; in three minutes the gum begins to fuse, on which, with a copper stirrer, the gum is cut and stirred about. If it feels lumpy and not fluid, and rises to the middle of the pot, it is lifted from the fire and stirred constantly until it goes down. Eight lbs. of copal occupies in general from sixteen to twenty minutes in fusing, from the beginning till it gets clear like oil. During the first twelve minutes, while the gum is fusing, the oil must be brought to a smart simmer, when it will be very nearly of the same temperature as the fused gum. On seeing an appearance of bubbling the boiling pot is lifted off and set on the ash bed, and 1½ gallon ladled out into a copper pouring jack, which is placed on the plate of the gum furnace to keep hot till wanted. When the gum is completely fused, it will again begin to rise in the pot in spite of all stirring to keep it down; when within 5 inches of the top, the hot oil is slowly and gradually poured in until towards the last, the stirring being kept up the whole time. In ten to twelve minutes, if the fire is strong and regular, the gum and oil will become quite clear. This is ascertained by dropping a little varnish on a piece of glass; if the globule appears clear and transparent, the oil and gum are properly mixed. One and a half gallon more oil is now taken from the boiling pot and placed in a copper jack on the plate of the gum furnace, and 1½ gallon in a spare tin ready for the third run. This leaves 3½ gallons of oil in the boiling pot. The maker now lifts the gum pot steadily, and placing its edge over that of the boiling pot, pours the contents gently into the oil, and holds the pot bottom upwards over the boiling pot for a minute to drain. A piece of thick carpet and an iron plate are kept in readiness to throw over the mouths of the vessels, should the oil catch fire.

The moment the gum pot is empty it is rinsed out with half a gallon of turpentine, wiped dry, and again placed on the fire with 8 lbs. more gum. This is treated precisely as before, and so with the third and last run. There will then be 24 lbs. gum and 8 gallons of oil in the boiling pot; heat is briskly applied until a scum rises and covers the surface of the contents, when it will begin to rise rapidly. When the mixture rises to near the rivets of the handles the pot is lifted off, conveyed to the ash bed and stirred down, the driers being at the same time scattered in by little at a time, if required; though the better plan is to secure rapid drying of the oil before making varnish of it, in which case no driers are required at this stage (see OIL, LINSEED). If the fire be good the quantities named will require to be boiled for three and a half to four hours from the time the last gum is in; but time is no criterion, as it may vary with the weather, the quality of the oil, the quality of the gum, the driers, the heat of the fire, &c. When the boiling has been continued long enough, a portion dropped on a glass plate will feel stringy between the fingers.

The pot is then carried to the ash bed, and left standing until cool enough to receive turpentine. If the gum is good and well run it may take as much as 15 gallons of turpentine, but if the gum was weak and badly fused 12 gallons may be too much. When, therefore, the latter quantity has been introduced, a little of the varnish is set aside in a saucer to cool; in a few minutes its consistency will show whether it requires more turpentine; if so, this is added. The varnish is then strained rapidly and stored in iron tanks to settle; when required for market it is dipped out from the top.

The foregoing general directions concerning the running of gum and pouring in the oil, and also boiling off and mixing, apply to the making of all kinds of oil varnishes—differences of the quantities and the qualities of oil and gum being of course considered.

The varieties of varnish are very numerous. A few well-tried recipes are given below as examples.

Amber Varnish.—Fuse 6 lbs., add 2 gallons of hot oil, boil until stringy, and add turpentine 4 gallons. The varnish is very durable, but dries slowly.

Cabinet Varnish.—Copal, 7 lbs.; drying oil, ½ gallon; turpentine, 3 gallons.

Copal Body Varnish.—Best gum, 8 lbs.; drying linseed oil, 2 gallons; turpentine, 3½ gallons.

Copal Carriage Varnish.—Gum, 8 lbs.; linseed oil clarified, 2½ gallons. Boil till very stringy, and add 5½ gallons turpentine.

When a faster drying varnish is required the above is added to a varnish composed of animé 8 lbs., clarified oil 2 gallons, and turpentine, 3½ gallons, in the proportion of two-thirds of the copal varnish to one-third of the animé varnish.

The use of driers is to be as much as possible avoided. If a good drying oil is used they are unnecessary. Nevertheless, many makers prefer to use linseed oil which has been simply heated, and in the boiling pot they then add ¼ lb. of white copperas, ¼ lb. of litharge, or sometimes both, to each run of gum and oil.

Oak varnishes are made with inferior gums. New Zealand kauri is now much used. The proportions are:—Gum, 8 lbs.; oil, 3 gallons; turpentine, 5½ gallons. The colour is given by adding a larger or smaller quantity of litharge, or using a darker gum.

Violette's Method.—Ten parts of copal and 20 parts of turpentine are heated to 350° C. in a closed vessel for fifteen to twenty minutes. On cooling, the gum

is found to be completely dissolved, and forms with the turpentine a bright, transparent, yellowish varnish. Ten parts of copal and 20 parts of linseed oil similarly treated form a liquid which only needs to be thinned with turpentine to form a varnish equal to the best coachmakers' varnish.

VIOLETTE proposed to treat the complete mixture of gum, oil, and turpentine, in the same way for the manufacture of varnishes. He says that 6 parts of copal, 2 parts of linseed oil, and 18 parts of turpentine, heated together to 350° C. in a close vessel, produce a good oil varnish. The vessels are subjected to a pressure of 20 atmospheres.

To attain the best results it is necessary to heat the gum to about 300° C., in order to drive off the 5 to 6 per cent. of water which it contains. The oil, or mixture of oil and turpentine, is then added, the vessel closed, and the heat continued until complete solution of the gum is effected. It is, of course, essential that the linseed oil be previously boiled, and the turpentine freed from water.

Amber requires a temperature somewhat higher than copal, about 400° C.

Gum copal and its congeners, and also amber, which are not naturally soluble in ether, turpentine, benzine, and other hydrocarbons, or in the vegetable oils, become soluble in them, both in the heat and cold, after they have been exposed in a close vessel to temperatures varying between 350° and 400° C., and the solutions thus made constitute true varnishes. The apparatus must be rigorously kept at a temperature varying between 350° and 400° C.

Amber treated with oil and turpentine by this process produces a clear pale varnish, such as no maker has hitherto been able to manufacture.

Copal and other refractory resins are soluble in oil of turpentine, &c., if they have been heated for fifteen to twenty minutes to 350° or 400° C. in closed vessels. The best way of operating is to heat the resin for a few minutes in an open vessel; 5 or 6 per cent. of water are by this means expelled. The vessel is then closed, and the heating continued. The product gives very excellent varnishes.

In France and Germany varnishes are made by processes based on that of VIOLETTE. The proportions used are much the same as those employed by English makers. The copal gum is inclosed, together with the requisite quantity of turpentine, in a copper vessel capable of bearing the pressure of twenty atmospheres, and heated to 400° C. The solution thus formed is mixed with linseed oil, which has been previously boiled till it has acquired the consistence of treacle. The varnishes work well, but dry somewhat slowly, and are deficient in the lustre and brilliancy characteristic of good English-made varnishes.

An analogous process is being tried in this country, but we are not able at present to give our readers such particulars as would enable them to produce varnishes.

Zingler's Varnish.—A mixture of 1 part of carbon disulphide, 1 part of camphor or turpentine, 1 part of benzine or rectified petroleum, and 2 parts of wood spirit, are heated in a close vessel; and powdered copal, or other gum added to the solvent in the proportion of 106 : 125 per 50 kilos. of resin. The mixture is allowed to stand for some days, and then linseed oil or a like drying oil is added.

Copal spirit varnish may be thus made by BÖTTGER'S method. Dissolve 1 part by weight of camphor in 12 parts of ether, then add 4 parts of copal finely powdered. As soon as the copal appears to be partly dissolved, and has become swollen, add 4 parts of strong alcohol or methylated spirits, and $\frac{1}{4}$ part of turpentine. After shaking the mixture and letting it stand for a few hours, a thoroughly good copal varnish is obtained.

Spirit Varnishes.—The gum is crushed and mixed with bruised glass, in the proportion of 2 lbs. of glass to 5 lbs. of gum, placed in a suitable vessel, with the requisite quantity of turpentine or other spirit, closely corked, and agitated by shaking by machinery or otherwise until the gum is dissolved. The varnish is then strained and stored in air-tight vessels. Steam heat is sometimes used.

Mastic Varnish.—Gum, 5 lbs.; turpentine, 2 gallons. Agitate in the cold.

Gum, $2\frac{3}{4}$ lbs. to each gallon of turpentine; heat very gently, with constant stirring: 8 lbs. of gum, with 4 gallons of turpentine, produce $4\frac{1}{2}$ gallons of varnish.

Paper Varnish.—Gum dammar or rosin, 10 lbs.; turpentine, 4 gallons. Heat gently (by steam, if possible), and strain while hot.

White Hard Varnish.—Sandarach, 5 lbs.; spirits of wine, 2 gallons. Agitate till dissolved, using bruised glass to assist the solution. A temperature of 80° Fahr. facilitates the process.

Brown Hard Varnish.—Sandarach, 3 lbs.; shellac, 2 lbs.; spirits of wine, 2 gallons.

Japan Varnish.—Copal, 7 lbs.; drying oil, $\frac{1}{2}$ gallon.

Shoes, &c., Jet Black Varnish for Leather (M. MARX).—Dissolve 10 parts of shellac in 5 parts of turpentine, add the mixture to 40 parts of methylated spirit in which 1 part of extract of logwood, and a little potassium bichromate and sulphate of indigo, have been already dissolved. Keep in well-stoppered bottles.

Dull Varnish.—A varnish which does not reflect light can be prepared by mixing a solution of a resin or gum with some liquid in which the resin or gum is insoluble. A mixture of 3 to 5 parts of sandarach dissolved in 48 parts of ether and $2\frac{1}{2}$ parts of benzol resembles ground glass when dry. A solution of gum dammar in resin, mixed with ether, also gives a good dull varnish: water renders this varnish semi-opaque. ARTHUR HUGHES recommends the following mixture :—

	Parts by weight.
Ether,	560
Benzol,	240
Sandarach,	40
Canada Balsam,	10

Colourless Copal Varnish.—The copal is carefully picked, each piece is broken, and a drop of rosemary

oil poured on it. Those pieces which on contact with the oil become soft are the ones used. The pieces selected are ground and passed through a sieve, being reduced to a fine powder. It is then placed in a glass vessel, and a corresponding volume of rosemary oil poured over it; the mixture is then stirred for a few minutes, until it is transformed into a thick liquor. It is then left to rest for two hours, when a few drops of rectified alcohol are added and intimately mixed; and this is repeated until the varnish is of a sufficient consistency. It then becomes bright and clear after standing for a few days.

Shellac Varnish.—An aqueous solution of gum lac can be made by boiling the crushed gum in a solution of carbonate of ammonia, until all ammoniacal odour has disappeared.

MÊNE dissolves by aid of heat 12 parts of best shellac and 4 parts of borax in 100 parts of water. This solution, after cooling, is poured into bottles, which should be well corked. The liquid may be employed as a varnish; or, mixed with oil of turpentine, added to oil paints to make them dry rapidly.

WATER.—Synonyms: *Eau*, French; *Wasser*, German; *Aqua*, Latin; ὕδωρ. Greek (H_2O).—Of all the materials concerned in the economy of the earth, water is, without doubt, one of the most important. Covering as it does, in the form of oceans, lakes, and rivers, more than two-thirds of the surface of our planet, it is evident that the condition of that surface is largely determined by it. The grouping of both flora and fauna is to a great extent governed by the arrangement of land and sea, and on this also depends the greater part of the locomotion of the world. Still, looking at the mechanical action of water, we find that this is not restricted to the ocean, but that the varied configuration of the surface of the dry land is chiefly due to the moulding force of water in the form of rain, rivers, and glaciers.

Although less obvious, the part it plays in animal and vegetable life is not less important. It constitutes seven-eighths of the weight of the human body, and of the bodies of many other animals, and upwards of nine-tenths of the weight of some plants. All the fluids of both plants and animals are aqueous solutions, and water is an indispensable constituent of the food of all living beings, serving as the universal vehicle for the conveyance of nourishment and the removal of waste. Without it, in the form of vapour and cloud in the atmosphere, life as at present constituted could not exist on our planet; for the direct rays of the sun would be insupportable during the day, and cold, consequent on uninterrupted radiation, equally fatal by night; but atmospheric water acts as a protection against both.

History.—From the earliest times water was considered as a simple substance, being one of the four elements of which the world was composed; the other three being fire, air, and earth. Many attempts had been made to penetrate its real nature; but as these were almost invariably conducted without the aid of measures or weights, and necessarily with the crudest and most imperfect apparatus, little information had been gained. It was generally thought that by repeated evaporation and distillation water could be obtained in the solid form; the facts on which this opinion was based being due to the almost invariable presence in water, as found in nature, of a greater or less quantity of solid matter in solution, which, not being volatile, would of course remain as a visible residue when the water was evaporated.

When the water employed did not contain such dissolved matter, similar results would often be obtained by reason of the solvent action of the water on the material of the vessel used for evaporation. This, although slow, would during the prolonged operations of the ancient philosophers dissolve a quantity of soluble matter, which on evaporation would leave a very substantial residue. It was reserved for CAVENDISH to prove, in the year 1781, that water was composed of two elements, and only two—oxygen and hydrogen.

Properties.—Water occurs in three states, as a gas, a liquid, and a solid. With certain reservations, which will be referred to hereafter, it occurs as a solid at all temperatures below 0° C., as a liquid under ordinary atmospheric pressure at temperatures between 0° and 100° C., and as a gas at temperatures above 100° C. It is, when pure, perfectly tasteless and odourless, and, when seen in small bulk, colourless. Large volumes exhibit, however, a distinct bluish-green colour, which may be seen when white light is transmitted through a long column of water, or through the solid ice of a glacier. When white light is reflected from the bottom of a lake or river of clear and pure water, as, for example, the Lake of Geneva, this colour is well seen; but if the depth be extreme the water appears black, the light being entirely absorbed. If it be turbid a green or yellow tint is observed; but a very slight turbidity often causes a deepening of the blue tint.

Water is almost incompressible, an increase of pressure, equal to one atmosphere, only reducing its volume to the extent of ·000045.—(OERSTED). Its specific heat is extremely high, and is used as a standard, the specific heat of all other substances being referred to it. A quantity of heat which would raise a given weight of water through a given range of temperature, would raise nine times that weight of iron, or thirty times that weight of mercury, through the same range.

Water is a bad conductor of heat, and if heat be applied to it from above, the surface layer only becomes heated, the heat passing downwards with extreme slowness; but if the heat be applied from beneath, that portion nearest the source of heat becomes expanded, and thus, being rendered specifically lighter, rises—its place being taken by a cooler, and therefore denser portion. A circulation is thus established by means of which the heat is rapidly and nearly uniformly distributed over the whole volume. This process is called *convection*, the heat being conveyed from one position to another by actual motion of the particles of water, and not by conduction.

The change of volume which water undergoes by change of temperature has been carefully studied, and presents a very remarkable phenomenon. Water is not always expanded by increase of temperature, having a point of maximum density from which it expands, whether its temperature be raised or lowered. This point occurs at 4° C. If heat be extracted from water at this temperature the volume increases steadily until it reaches the freezing point, 0° C., when it occupies a space about $\frac{1}{1000}$th greater than at 4° C. Arrived at this point it solidifies, and in doing so undergoes a sudden expansion, equal to nearly one-eleventh of its volume.

This expansion on freezing is a powerful agent for the breaking up of rock masses, the water permeating their interstices in the liquid form, and, on solidifying, rending the mass asunder. Frequent oscillations of temperature rapidly bring about the complete disintegration of the hardest rocks. The bursting of pipes used for conveying water is occasioned in the same way. It follows from this that water, when cooled from the surface below 4° C., becomes specifically lighter, remains at the top, and being a bad conductor of heat, the lower portions are protected; so that the temperature of a large volume of water, as of a river or lake, cannot be reduced below 4° C. except with extreme slowness. Ice, of course, has a still greater floating power.

If water taken at its maximum density be heated, instead of cooled, it expands steadily as the temperature rises, until it reaches the boiling point, 100° C., when, if the atmospheric pressure be normal, it is converted into vapour, which, at the same temperature, occupies a volume equal to 1696 times that occupied by the water from which it is formed.

The expansion of water by heat between 0° C. and 100° C. has been very carefully investigated by KOPP (*Pogg. Ann.* lxxii., 1 and 223), and the results are given in the subjoined table.

The following interpolation formulæ are derived from the numbers in the second column of the table. V is the volume at the temperature $t°$ C. of a quantity of water whose volume at 0° C. = 1:—

Between 0° and 25° C.

$$V = 1 - 0{\cdot}000061045t + 0{\cdot}0000077183t^2 - 0{\cdot}00000003734t^3.$$

Between 25° and 50° C.

$$V = 1 - 0{\cdot}000065415t + 0{\cdot}0000077585t^2 - 0{\cdot}0000000354081t^3.$$

Between 50° and 75° C.

$$V = 1 - 0{\cdot}00005916t + 0{\cdot}0000031849t^2 - 0{\cdot}0000000072848t^3.$$

Between 75° and 100° C.

$$V = 1 - 0{\cdot}00008645t + 0{\cdot}0000031892t^2 - 0{\cdot}0000000024487t^3.$$

By means which will be referred to later, water may be cooled below zero without solidifying, and it is found that as the temperature falls it continues to expand strictly in accordance with the table. Similarly water may be heated above 100° C. without ceasing to be a liquid, and the expansion continues regularly. Ice behaves like other solids when heated, its specific gravity at —19° C., being 0·92013, and at 0° C. 0·918; so that it expands when heated, its co-efficient of expansion being 0·000122 for 1° C.

EXPANSION OF WATER BY HEAT (KOPP).

Temperature.	Vol. at 0° = 1.	Dens. at 0° = 1.	Vol. at 4° = 1.	Dens. at 4° = 1.
Degrees C.				
0	1·00000	1·000000	1·00012	0·999877
1	0·99995	1·000053	1·00007	0·999930
2	0·99991	1·000092	1·00003	0·999969
3	0·99989	1·000115	1·00001	0·999992
4	0·99988	1·000123	1·00000	1·000000
5	0·99988	1·000117	1·00001	0·999994
6	0·99990	1·000097	1·00003	0·999973
7	0·99994	1·000062	1·00006	0·999939
8	0·99999	1·000014	1·00011	0·999890
9	1·00005	0·999952	1·00017	0·999829
10	1·00012	0·999876	1·00025	0·999753
11	1·00021	0·999785	1·00034	0·999664
12	1·00031	0·999686	1·00044	0·999562
13	1·00043	0·999572	1·00055	0·999449
14	1·00056	0·999445	1·00068	0·999322
15	1·00070	0·999306	1·00082	0·999183
16	1·00085	0·999155	1·00097	0·999032
17	1·00101	0·998992	1·00113	0·998869
18	1·00118	0·998817	1·00131	0·998695
19	1·00137	0·998631	1·00149	0·998509
20	1·00157	0·998435	1·00169	0·998312
21	1·00178	0·998228	1·00190	0·998104
22	1·00200	0·998010	1·00212	0·997886
23	1·00223	0·997780	1·00235	0·997657
24	1·00247	0·997541	1·00259	0·997419
25	1·00271	0·997293	1·00284	0·997170
26	1·00295	0·997035	1·00310	0·996912
27	1·00319	0·996767	1·00337	0·996644
28	1·00347	0·996489	1·00365	0·996367
29	1·00376	0·996202	1·00393	0·996082
30	1·00406	0·996008	1·00423	0·995787
35	1·00570			
40	1·00753			
45	1·00954			
50	1·01177			
55	1·01410			
60	1·01659			
65	1·01930			
70	1·02225			
75	1·02541			
80	1·02858			
85	1·03189			
90	1·03540			
95	1·03909			
100	1·04299			

Water is volatile at all temperatures, vapour being formed on the surface of ice far below the freezing point. The force exerted by this vapour depends upon the temperature, and is called its "tension," being very small at low temperatures, but increasing rapidly as the temperature rises. The vapour tension of water at different temperatures has been determined by REGNAULT with extreme accuracy. It is usually expressed as equal to the pressure of a column of mercury of a certain length measured in millimetres, and was determined by introducing a quantity of water into the Torricellian vacuum in the upper part of a barometer, and noting the extent to which the mercurial column was depressed at different temperatures; the depression being due to the pressure exerted by the vapour of the water on the surface of the mercury in the tube. By suitable modifications of the apparatus the inquiry was extended to temperatures much above 100° C. The table on next page is obtained from these experiments.

So long as the vapour tension is less than the pressure on the surface of the liquid, the evaporation takes place wholly from the surface; but when these forces become equal, bubbles of vapour are formed

in the liquid and rise to the surface, producing the phenomenon of *ebullition* or *boiling*, and the temperature at which this occurs is called the boiling point. As this depends on the pressure, it may take place at all temperatures, and with a good air-pump water may be made to boil at 20° C., and by heating it in a strong vessel with a heavily-weighted safety valve, its boiling point may be raised to a degree only limited by the strength of the vessel. At the normal pressure of the atmosphere — when the barometer indicates 760m.m. of mercury at 0° C.—water is said to boil at 100° C., its boiling point under these conditions being in fact taken as the standard by which thermometers are graduated. Atmospheric pressures are also sometimes ascertained by observing the temperature as indicated by a good thermometer at which pure water boils. On the summit of Mont Blanc the boiling point of water was found, by Dr. Frankland, to be 84°·7 C. (184°·5 Fahr.). When ice is slowly heated its temperature, as indicated by a thermometer, rises until liquefaction commences, but then remains constant until the whole of the ice is melted. The heat applied during this interval is said to become latent, and is consumed in effecting the change from the solid to the liquid state of the water. The amount of heat required to convert a given weight of ice into water at the same temperature would, according to Regnault, Provostaye, and Desains, be sufficient to raise the temperature of an equal weight of water 79° C. The amount of heat required to liquefy ice being so great, and the temperature of liquefaction so constant, renders this point extremely convenient as a standard of reference, and it is chosen as the zero of the centigrade thermometric scale.

TENSION OF AQUEOUS VAPOUR (REGNAULT).

Temperature.	Tension in Millimetres of Mercury.	Temperature.	Tension in Millimetres of Mercury.	Temperature.	Tension in Millimetres of Mercury.
Deg. C.		Deg. C.		Deg. C.	
—32	0·320	19	16·346	105	906·41
—30	0·386	20	17·391	110	1075·37
—25	0·605	21	18·495	115	1269·41
—20	0·927	22	19·659	120	1491·28
—15	1·400	23	20·888	125	1743·88
—10	2·093	24	22·184	130	2030·28
—5	3·113	25	23·550	135	2353·73
0	4·600	26	24·988	140	2717·63
+ 1	4·940	27	26·505	145	3125·55
2	5·302	28	28·101	150	3581·23
3	5·687	29	29·782	155	4088·56
4	6·097	30	31·548	160	4651·62
5	6·534	35	41·827	165	5274·54
6	6·998	40	54·906	170	5961·66
7	7·492	45	71·391	175	6717·43
8	8·017	50	91·982	180	7546·39
9	8·574	55	117·478	185	8453·23
10	9·165	60	148·791	190	9442·70
11	9·792	65	186·945	195	10519·63
12	10·457	70	233·093	200	11688·96
13	11·162	75	288·517	205	12955·66
14	11·908	80	354·643	210	14324·80
15	12·699	85	433·041	215	15801·33
16	13·536	90	525·450	220	17390·36
17	14·421	95	633·778	225	19097·04
18	15·357	100	760·000	230	20926·40

As soon as the whole of the ice is melted the temperature again begins to rise, and continues to do so until the boiling point is reached, when it once more becomes stationary until the whole of the water is converted into steam. The heat applied here also becomes latent, the steam escaping freely from the water, and having the same temperature as the water itself. The heat required to convert a given weight of water at the boiling point into steam would, according to Regnault, raise the temperature of an equal weight of water 537° C., or what amounts to the same thing, would raise the temperature of 537 times that weight of water 1° C. When the whole of the water is converted into steam the temperature again rises. This succession of phenomena can be exactly reversed. If a quantity of steam, at a temperature above 100° C., be cooled, the temperature falls until it reaches 100° C., when liquefaction commences, and the temperature is stationary until the whole of the steam is condensed, a quantity of heat being given out precisely equal to that which was rendered latent in converting the water into steam. The temperature of the water thus formed falls steadily until it reaches 0° C., when ice begins to appear, and the temperature is stationary until the whole is solid, the amount of heat evolved being equal to that rendered latent in previously melting the ice.

It has been mentioned that, under certain conditions, water can be cooled below 0° C. without solidifying. This is the case when the water has been previously boiled to expel air or other dissolved gases, and then cooled very slowly and without agitation. In this way Dufour succeeded in cooling water to —20° C. without solidification. Contact with a solid body, or the slightest agitation, generally causes immediate partial solidification, the latent heat thus liberated raising the temperature, both of the ice and water, to 0° C. But although water can be cooled below zero in this way, ice cannot be heated *above* zero; hence the melting point of ice is always constant at ordinary pressures. By a greatly increased pressure it is slightly depressed. In a similar manner water may be heated above its proper boiling point without being converted into steam. This depends chiefly on the condition of the surface of the vessel in which it is placed; in a smooth and perfectly clean open glass vessel it may often be heated to 5° or 6° above the boiling point. When ebullition at last occurs it is almost explosive in its violence, a large volume of steam is formed, and the temperature of both water and steam falls to the boiling point, the excess of heat being rendered latent in the steam. In a metallic vessel the boiling point is very constant when the pressure does not vary.

Water in the solid state, or ice, is like that in the liquid state, a bad conductor of heat; and since the particles are not free to move, this property is not obscured by the transference of heat by convection. Ice is a crystalline body, belonging to the hexagonal system, as may be seen by transmitting a beam of heat-rays through a clear slab of ice, when internal liquefaction will take place generally in a number of separate localities, each exhibiting an hexagonal cavity partly filled with liquid water. As

water on passing from the solid to the liquid state contracts, the water formed by liquefaction of the ice is not of sufficient volume to entirely occupy the place of the ice; hence each cavity contains a small space filled with watery vapour only.

Water, both in the solid and liquid states, is a bad conductor of electricity. When two pieces of melting ice are brought in contact they readily unite to form a single piece: this phenomenon is termed *regelation.*

Snow consists of hexagonal crystals of ice, generally arranged in star-like clusters, with six rays symmetrically bestowed, and often of remarkable beauty. When submitted to considerable pressure at the freezing point, snow is converted into solid and transparent ice.

Steam or water vapour is colourless, transparent, and invisible. The visible clouds, commonly called steam, are really composed of minute globules of *liquid* water, produced by the partial or complete condensation of the steam. When a current of steam is allowed to escape with considerable force into the atmosphere, a small transparent space will be seen near the orifice from which it issues, the uncondensed steam passing invisibly across this space.

The specific gravity of water vapour at 100° C. is less than two-thirds of that of air at the same temperature. Steam, like all gases, is a bad conductor of heat; but heat is distributed through it readily by convection. Radiant heat, according to Tyndall, is rapidly absorbed by water vapour; but this has has been disputed by Magnus. Tyndall estimates that at least 10 per cent. of the entire terrestrial radiation is absorbed by the aqueous vapour which exists within 10 feet of the earth's surface on a day of average humidity. This absorptive power is much greater for obscure than for luminous rays, so that the solar heat reaches the earth more readily than heat leaves the earth by radiation into space, and hence the aqueous vapour present in the atmosphere maintains the earth's surface at a higher temperature than it would otherwise possess. Like all good absorbers, water vapour is also a good radiator, and heat is largely dissipated in space by the upper layers of aqueous vapour. Water in the liquid form is a remarkably powerful absorbent, a layer only one-fiftieth of an inch in thickness arresting 80 per cent. of the heat radiated from red-hot platinum.

Chemical Properties.—Water is formed by the combination of two volumes of hydrogen with one volume of oxygen, or of 2 parts by weight of the former with 16 parts of the latter. In the act of combining condensation takes place, so that the three volumes of mixed gases before their union produce only two volumes of water vapour or steam at the same pressure and temperature. This constitution of water may be shown in several ways.

If a voltaic current be passed through a mixture of water and sulphuric acid, the water is decomposed and a gas is freely produced at each pole, that at the negative pole having twice the volume of that at the positive. The former consists of hydrogen, and the latter of oxygen.

If a white-hot ball of platinum be plunged into water, a mixture of the same gases is produced by the decomposition of the water; and this mixture on analysis will be found to contain one volume of oxygen and two volumes of hydrogen.

In these operations both of the constituents are set free. There is, however, a large class of decompositions in which only one is liberated, the other remaining in combination with some other substance. When potassium or sodium is thrown on to water an energetic action takes place; the water is decomposed, one-half of the hydrogen being liberated, whilst the other half, and the whole of the oxygen, combine with the metal to form a hydrate—

$$2OH_2 + Na_2 = 2ONaH + H_2.$$

When steam is passed through an iron or porcelain tube filled with iron turnings and heated to redness, the iron becomes coated with a film of the black or magnetic oxide of iron, produced by the union of the iron with the oxygen of the water-vapour, the hydrogen being set free—

$$4OH_2 + Fe_3 = Fe_3O_4 + 4H_2.$$

When a solution of chlorine in water is exposed to direct sunlight the water is decomposed, hydrochloric acid being formed and oxygen liberated—

$$Cl_2 + OH_2 = 2HCl + O.$$

The composition of water may also be demonstrated synthetically. If two volumes of hydrogen be mixed with one volume of oxygen in a strong vessel, and an electric spark be passed through the mixture, rapid combustion will take place; and if the temperature be above 100° C. the vessel will be found to contain, in place of the hydrogen and oxygen, two volumes of steam or water vapour, measured at the same temperature and pressure. If an excess of either constituent above the proportions just stated be used, this excess will remain mixed with the water vapour.

If a stream of hydrogen be passed through a tube filled with oxide of copper and heated to redness, the oxide will be decomposed, the oxygen combining with the hydrogen to form water, and the copper being set free. In this way Dumas determined the composition of water with great accuracy. The hydrogen was produced by the action of dilute sulphuric acid on purified zinc, and to remove impurities was passed through tubes containing acetate of lead, sulphate of silver, caustic potash, and phosphoric anhydride, the last removing every trace of water. The stream of gas was then passed over the heated oxide of copper, and lastly through an empty flask and tubes containing respectively chloride of calcium and oil of vitriol, the water produced being retained in these vessels. The bulb containing the oxide of copper was accurately weighed before and after the experiment, as were also the empty flask and drying tubes. The loss of weight of the former indicated the weight of oxygen which had combined with the hydrogen to form the quantity of water which had increased

the weight of the empty flask and drying tubes. For every 8 parts by weight of oxygen thus employed, it was found that 9 parts of water had been formed, and the water was, therefore, composed of 8 parts of oxygen and 1 of hydrogen—

$$CuO + H_2 = Cu + OH_2.$$

Water is formed whenever hydrogen, or a substance containing it, is burned in oxygen or heated in contact with substances which easily supply oxygen.

Water combines with many other substances in several ways. It unites with anhydrides to form acids; as, for example, with sulphuric or nitric anhydride to form sulphuric or nitric acid—

$$OH_2 + SO_3 = SO_4H_2;$$
$$OH_2 + N_2O_5 = 2NO_3H.$$

With many metallic oxides it forms hydrates, as with potassic oxide and quick lime—

$$OH_2 + OK_2 = 2OKH;$$
$$OH_2 + CaO = CaH_2O_2.$$

The cases mentioned above, and the classes of reactions which they represent, are commonly called atomic combinations *par excellence*, and are accompanied by the evolution of heat, the combinations taking place in constant and definite proportions. The water entering thus into combination is not supposed to exist, as water, in the compound formed.

Water also unites with other substances as water of crystallization; it is here assumed to exist as water in the compound formed, and the combination is said to be molecular as distinguished from atomic, the symbols representing the water being divided in the formula from the other symbols by a comma—thus, $CO_3Na_2,10OH_2$. In these unions heat is generally, if not invariably evolved, and the combination takes place in definite proportions. Example—

$$SO_4Na_2 + 10OH_2 = SO_4Na_2,10OH_2;$$
$$PO_4Na_2H + 12OH_2 = PO_4Na_2H,12OH_2;$$
$$B_4O_7Na_2 + 10OH_2 = B_4O_7Na_2,10OH_2.$$

In most cases a part of the heat evolved is due to the change of state which the water undergoes in passing from the liquid to the solid form. It is, in many cases, difficult to distinguish between the so-called molecular and atomic combinations.

Lastly, water unites with other bodies by dissolving or mixing with them. The proportions between the two substances are indefinite, taking place in some cases in all proportions without limit, as, for example, in the case of alcohol and water; and, in other cases, in all proportions within certain limits—thus, 100 parts of water will dissolve at 15° C. 25 parts of potassic nitrate, or any less quantity. This action is not usually accompanied by the evolution of heat, the temperature being often depressed. When a solid body is dissolved this absorption of heat is often very great, a large proportion of heat being rendered latent by the liquefaction of the solid. Thus, when sulphuric acid is mixed with snow, a powerful freezing mixture is obtained, owing to the large amount of heat rendered latent in the passage of the snow to the liquid state. The solubility of bodies is largely affected by changes of temperature; as a general rule the quantity of solid substance dissolved increases as the temperature is increased, but there are a few cases in which the reverse occurs. Water also dissolves many gases, and here the solubility, as a rule, varies *inversely* as the temperature, and solution is often attended with evolution of heat, due to the change from the gaseous to the liquid state.

Water Analysis.—Water as it occurs in nature is never pure. It is contaminated by impurities derived from the air, in which it floats as cloud, and through which it falls as rain, and from the rocks and soil over and through which it passes on its way to the ocean. These impurities greatly affect the value of the water for drinking, cooking, cleansing, or manufacturing purposes; and it is the object of the analyst to ascertain more or less completely, according to the purpose for which the water is to be used, their character and proportions. It will be convenient to classify the various kinds of natural waters under the following heads:—Rain water; upland surface water; surface water from cultivated land; shallow well water; deep well water; spring water; and sea water: and to these natural waters must be added an important class of artificial waters, viz., sewage or town drainage. The usual character of the impurities in these great classes of waters may be briefly stated as follows:—Rain water contains a very small proportion of mineral matter, with a considerable proportion of organic matter. Upland surface water contains usually a much larger proportion both of mineral and organic matter, the mineral matter being largely influenced, both as to quantity and quality, by the geological character of the rocks* over or through which the water has passed; the nature and amount of the mineral impurity being dependent on the soluble constituents of the rock.

In surface water from cultivated land the quantity, both of mineral and organic matter, is usually larger than in rain water, the organic matter being especially augmented in quantity; and the influence of the geological character of the district is, to a great extent, obliterated by the application of various manures in the operations of agriculture.

In shallow well water the impurity of all kinds is, as a rule, greatly increased—a fact sufficiently explained by the consideration, that a shallow well is essentially a pit for the reception and accumulation of drainage from the surrounding soil; that for convenience of access it is almost always made close to the dwelling which it is to supply with water; that the soil in the vicinity is therefore inevitably the recipient of various kinds of household waste; and last, but not least, that similarly for convenience

* The term *rocks* is here used in its geological sense, and includes the whole substance of the earth, whatever may be its nature or texture; granite and loose sand being equally called *rocks*.

of access another shallow pit is usually constructed near the house and used as a cesspool. The effect of the geological character of the soil is generally quite obliterated by this local impurity. Such water, although often most disgustingly contaminated, is usually bright, sparkling, and palatable, the saline flavour due to salts in solution, and which is sometimes very pronounced, being often much approved by those who are accustomed to it.

Deep well waters frequently contain considerable quantities of mineral matter, but almost invariably very little organic matter, this having been removed by oxidation in passing through a great depth of porous rock. The separation of deep from shallow wells must necessarily be arbitrary, and for our purpose wells are said to be deep the water of which is drawn from a bed not less than 100 feet from the surface. In cases where the well passes through a watertight stratum, such as a bed of clay, it may be considered as *deep* even when the actual depth of the shaft is much less than 100 feet, since the water taken from below such a septum must pass through a very considerable mass of rock, and thus be fully subjected to filtration, if not to oxidation. In all cases surface drainage must be carefully excluded from the shaft. The character of deep well waters is strongly influenced by the geological nature of the rock from which the water comes.

Spring waters closely resemble the preceding class, their conditions being almost identical. In fact, deep wells may be viewed as artificial springs.

In sea water the most noteworthy characteristic is, of course, the enormous proportion of mineral matter in solution, amounting to about 4000 parts per 100,000 parts of water. The organic matter present is large as compared with that in fresh water, and very highly nitrogenous.

In sewage the variations are extreme; but the organic matter present is usually of large amount, as is also the ammonia. Nitrates and nitrites are rarely found, having been in most cases destroyed by the large quantity of putrefying organic matter. The quantity of chlorine present is usually very significant, being derived almost exclusively from urine.

The problem presented to the analyst is this:—By an examination of the impurities in a sample of water, and by a consideration of the known facts respecting the source of the water, to ascertain its history and character, and whether it is liable to serve as a vehicle for the transmission of disease.

Collection of Samples.—As some of the impurities, although important, are present in very small quantity, it is necessary to take great care in collecting samples of water for analysis, to avoid accidental pollution and to secure a truly representative sample. Stoneware jars should not be used, as they impart various mineral matters to waters contained in them. Corks should also be avoided, if possible; and if they must be used, they should be quite new and well washed with the water itself before insertion into the bottle. Stoppered glass bottles should in all cases be used if they can be obtained. Those known as "Winchester quarts" (holding about two imperial quarts), to be had from any druggist, are very convenient. They should be perfectly clean, and it is desirable that they should not have been used for any other purpose. In collecting the sample, first fill the bottle completely with the water; then, having poured this away, rinse the bottle three times with the water, filling it each time about one-third full. Then fill it nearly to the stopper, insert the stopper, tie a piece of calico tightly over it, and seal the string.

If the sample be taken from a pump, this should first be worked until the water which has been standing in the pump and pipe has been removed, and the water should then be allowed to flow directly from the spout of the pump into the bottle. Similarly, if the sample be taken from a tap, the water which has been stationary in the tap and service-pipe should first be allowed to run off, and then the bottle filled directly from the tap. If the sample is to represent a town supply it should be taken from a pipe in direct communication with the street main, and not from a cistern. In taking a sample from a tank, well (without pump), or stream, plunge the bottle completely below the surface, if possible. If a can or dipper be used, a thin copper wire for drawing it up should be employed: both must be scrupulously clean, and in all cases avoid as much as possible collecting water from the surface, or disturbing any mud or sediment at the bottom.

For ordinary sanitary analysis, collect of sewage, water from polluted rivers and streams, and shallow wells, one Winchester quart; of water from deep wells, ordinary unpolluted rivers, streams, and springs, two Winchester quarts; and of water from lakes and tarns, and mountain springs and streams, or other very pure sources, three Winchester quarts. If a more detailed analysis is required, a proportionately large volume of water will be necessary.

At the time of collection note the following particulars:—The source of the sample—from a well, river, stream, &c., giving its proper local name, if it have one, or sufficient description to effectually identify it. If it is from a well, describe the soil and subsoil, and the water-bearing stratum into which the well is sunk; the depth and diameter of the well, and its distance from cesspools or drains, or other sources of pollution; and state whether the well does or does not pass through a bed of clay or other impervious stratum, and if so, whether its shaft is watertight above that stratum. If the sample is from a river or stream, state the distance from the source to the point of collection, and whether sewage or other animal polluting matter is known to have access to the stream above that point. If from a spring, describe the stratum from which the spring issues, and whether the sample is taken direct from the spring or otherwise.

Preliminary.—To preserve at all times the representative character of the sample, it should be made an invariable rule to shake the bottle before removing any portion of its contents. Unless this is

done the proportion of suspended matter, if any, will be continually changing.

The appearance of the water as to colour and clearness, or the reverse, should be noted. Colour is best seen when the water is placed in a tall cylinder of clear colourless glass, placed on a white surface. A similar vessel, filled with distilled water to a similar depth, should be used for comparison. For observation of clearness the water should be seen in a large, nearly spherical flask, held between the eye and a good source of light. The light should not, however, be unobstructed, but the flask should be so held as to have an opaque object, such as a part of the window-sash, between it and the light, in a line drawn from the eye through the centre of the flask. Thus arranged, any matter in suspension will be seen on a dark ground as objects are seen in a microscope with dark ground illumination. This observation is very conveniently made when measuring out the portion for determination of organic carbon and nitrogen. If the sample be turbid, the question whether it is to be filtered or not before analysis must now be determined.

If the amount of suspended matter is to be estimated the water should be filtered before determination of total solid residue, organic matter, and ammonia. The suspended matter is of importance chiefly in the cases of river, lake, and spring waters, and town supplies. If the turbidity is due to some exceptional or temporary cause, such as repairs to the conduit, or the newness of the well, it is seldom necessary to determine the suspended matter, but the water should be filtered before analysis. If the temporary turbidity is due to admixture of *organic* matter, the analysis would scarcely be worth making in most cases. In some instances it is desirable to examine the suspended matter microscopically. For this purpose about a litre of the turbid water should be placed in a tall glass cylinder, and left at rest for twelve to twenty-four hours. When the suspended matter has fallen to the bottom, all the water, except about 20 or 30 c.c., should be poured off by slowly and steadily tilting the vessel, care being taken that the motion be steady and without jerks. The small quantity remaining will contain almost the whole of the suspended matter, and should be placed in a smaller vessel at rest, so that the solid matter may again subside. Samples can then be taken up with a clean dipping tube, and placed on a glass slide for examination under a microscope, in the usual way.

To examine the water for *taste* and *odour* it should be heated to about 30° to 35° C.

Determination of Total Solid Matters.—A platinum basin is heated to redness, allowed to cool under a desiccator, and weighed. It is then placed on a steam or water bath, and a measured quantity of the water evaporated to dryness in it. For shallow well waters 250 c.c. is a convenient quantity to use; for sewages, 100 c.c.; for waters containing more than 0·1 part of ammonia per 100,000 parts, 100 c.c.; and for other waters, 500 c.c. In the case of sewages, and waters containing more than 0·1 part of ammonia, the residue is not used for the determination of nitrogen as nitrates and nitrites, and therefore it is only necessary to consider what quantity of water will leave a residue convenient to weigh; while in the other cases the volume taken should be that which will be convenient for the determination of nitrogen as nitrates and nitrites. The platinum basin should be supported on the bath in a glass ring with a flange on its upper edge. The top of a beaker of suitable size, cut off at about 20 m.m. from the edge, answers admirably. At the end of the evaporation, the outside of the basin is wiped dry with a clean cloth, and it is placed in a steam or water oven at 100° C. for about three hours. It is then allowed to cool under a desiccator, weighed as rapidly as possible, and returned to the bath. After an hour it is again weighed, and so on, until between two successive weighings, with not less interval than an hour, it has lost less than a milligramme in weight.

The final weight, minus that of the empty dish, gives the weight of the total solid matter in the quantity of water used. The total solid matter is chiefly of importance with reference to the employment of the water in steam-boilers, and for similar purposes. River water usually contains from 10 to 40 parts; deep well and spring water from 20 to 70 parts, but sometimes considerably more; shallow well waters vary within a very wide range, containing from 30 to 150 parts, and not unfrequently still more, the quantity being determined generally by local conditions of pollution; sewage usually contains from 50 to 100 parts, but frequently much more, and sometimes less, the proportion depending generally on the ratio of the water supply to population. As a rule, but not invariably, the total solid matters exceed in quantity the sum of the constituents determined; the nitrogen, as nitrates and nitrites, being calculated as potassic nitrate, and the chlorine as sodic chloride.

Determination of Organic Carbon and Nitrogen.—There is no method at present known by which the actual amount of organic matter present in water can be ascertained; but the following method, which was first described by Drs. Frankland and Armstrong, in the *Journal of the Chemical Society*, March, 1868, enables us to determine with very considerable accuracy the quantities of the two principal constituents—carbon and nitrogen—yielded by that organic matter on combustion. Since its first publication no essential variation has been made in the process; but some modifications have been introduced which greatly facilitate manipulation and increase its accuracy, and these are embodied in the following description.

A quantity of the water, a litre or less according to circumstances, is measured out and poured into a flask in which it can be conveniently boiled. The quantity taken is usually determined by the amount of ammonia which the water contains, according to the following scale:—If it contains less than 0·05 part of ammonia per 100,000 parts, a litre should be used; up to 0·2 part, half a litre; up to 1 part, a quarter of a litre; and above 1 part, 100 c.c., or less. If it has been decided to filter the sample,

care must be taken, as in the estimation of ammonia, that the filter paper used is free from ammonia, unless the quantity of ammonia present is very large. If the sample is also to be filtered for the estimation of ammonia, the same filter should be used. Add to the measured quantity thus taken 15 c.c. of a saturated solution of sulphurous acid, and boil briskly for about half a minute to decompose carbonates. The sulphurous acid gas should be prepared by the action of sulphuric acid upon metallic copper; it should be washed by passing through water, and then passed into water free from ammonia and organic matter, until a saturated solution is obtained. This water, free from ammonia and organic matter, is prepared by boiling ordinary distilled water with 1 gram of potassic hydrate and 0·2 gram of potassic permanganate per litre for twenty-four hours under an inverted condenser, and then distilling over until 100 c.c. of the distillate, placed in a deep glass cylinder on a white surface, with 1 c.c. of Nessler's solution (*see* Determination of ammonia), exhibits no yellow tinge after standing for five minutes. The remainder is distilled over (stopping short of dryness) slightly acidified with pure sulphuric acid, and redistilled from a glass retort for use.

The water thus boiled with sulphurous acid is then evaporated to dryness in a hemispherical glass dish without a lip, and about a decimètre in diameter. The water in the flask must be kept warm, in order to avoid cracking the glass dish when it is filled up from time to time as the evaporation proceeds. The flask should be covered with a watch glass, or better, with an inverted beaker. The glass dish is placed in a copper dish with a flange with upturned edge (*e*, *f*, *g*, Fig. 1), the diameter of which across the flange is about 14 centimètres, the concave part being shaped to fit the outside edge of the glass dish (*d*) closely. The flange slopes slightly towards the centre, and at one point in the rim a small lip is formed. The copper dish is placed on a steam-bath, and the flange supports a tall, thin, glass shade, *i*, about 30 centimètres high. As the evaporation proceeds, the vapour is condensed on the inside of the shade, and runs down into the copper dish, filling the space between it and the glass dish, and thus efficiently conveying heat to the latter. It finally passes off by the lip, in which a piece of tape should be placed just under the edge of the shade to lead it to a vessel placed to receive it. If the sample is likely to contain a considerable quantity of nitrates, add to the first dishful two or three drops of a solution of ferrous or ferric chloride, which must be free from ammonia or organic matter; and if it does not contain much carbonate add also one or two c.c. of a saturated solution of hydric sodic sulphite, which has been prepared by passing sulphurous anhydride into a solution of recently ignited sodic carbonate.

Bischoff has effected an important improvement in this apparatus, which is shown in Fig. 1, and which, by automatically feeding the water into the dish as the evaporation proceeds, greatly reduces the time required; since, needing no personal attention, the evaporation may be continued during the night. On the copper dish, *e*, just described, stands a ring, *e*, *h*, of stout sheet copper, about 80 m.m. in height, and slightly conical, the upper part being the narrower. Round its upper edge it has a narrow flange,

Fig. 1.

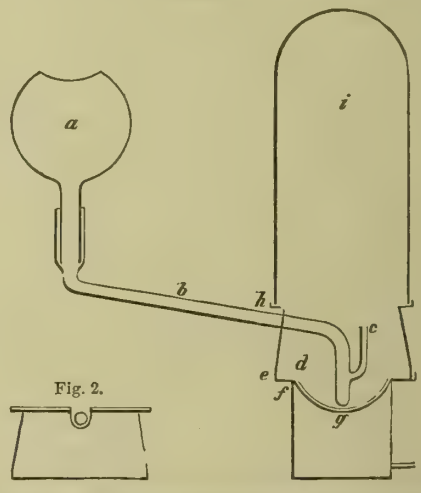


Fig. 2.

h, of the same external diameter as the copper dish, *e*, and with a similar vertical rim. The glass shade, *i*, stands securely on either the ring or the dish. In its upper edge, cutting through the flange, the ring has a small notch or slot, shown in Fig. 2, through which passes the inclined glass-delivery tube, *b*, the lower end of which, at *g*, opens at the bottom of the dish, *d*, and carries a narrow air-tube, *c*, the upper end of which is open above the edge of the dish, *d*. The upper end of the delivery-tube is ground to fit over the neck of the flask, *a*, which contains the water to be evaporated. The flask is supported in the ring of a retort stand (not shown in the figure), and a slot being cut in the ring to admit of the passage of the neck of the flask. To use this apparatus the glass dish is placed in position on the copper dish, *e*, *f*, *g*, with ferrous chloride and sodic sulphite added, if required. The copper ring is next adjusted, and then the water is boiled with sulphurous acid, either in the flask, *a*, and allowed to cool; or it may be boiled in another flask, and afterwards transferred. When nearly cold the delivery tube is carefully fitted into the neck of the flask, and the whole inverted with a steady, not too rapid motion, so that the end of the delivery tube rests in the glass dish, as in the figure, the tube passing through the slot in the copper ring, and the flask being supported on the retort stand. If the delivery tube fits well there is no need to give any separate support to it, provided that it and the neck of the flask are at about the same temperature when put together. Lastly, the shade is fitted on, and the evaporation proceeded with. Whenever the level of the liquid in the glass dish falls below the point at which the air-tube, *c*, joins the delivery tube, a bubble of air enters from *c* and passes up the tube into the flask, an equal volume of water

passing into the dish. As soon as the flask and delivery tube are empty they should be removed, any solid matter adhering to the end of the delivery tube washed into the dish with a few drops of water, the copper ring removed, and the glass shade placed on the copper dish, *e*, *f*, *g*. The evaporation is then carried to dryness as usual.

In Bischoff's apparatus the supply passes from the reservoir to the evaporating dish through a straight tube. There is, consequently, convection through this tube to the reservoir, and that is necessarily attended with much loss of heat. It is, moreover, objectionable to heat the delicate organic matter of waters (and especially of peaty waters) any longer than is strictly necessary. To avoid these evils Dr. E. Mills has contrived a convectionless feed. Its principle is very simple. The delivery tube, instead of being straight, is slightly bent in two places, so that, at the end of each regurgitation, two long bubbles of air always remain entrapped. Between these and the tube the layer of water is so thin that convection becomes impossible. The heat that would otherwise escape is thus locked up within the evaporator, and the water to be analysed is not heated until the last moment. So effectually is convection arrested that, with the first made (and rather imperfect) feed of this kind, and a rate of evaporation considerably exceeding 100 cubic centims. an hour, it took four hours for some rather strong hydrochloric acid in the dish to redden blue litmus in the reservoir.

With waters containing much ammonia (more than 0·1 part per 100,000), and with sewages, a simpler method is sufficient. They may be evaporated in a glass dish, placed on a steam or water bath and covered with a drum of filter paper, something like a small tambourine, made by stretching filter paper between two hoops of light split cane, the one being thrust into the other. The water in the flask, from which the dish is from time to time filled up, must be kept warm, as before mentioned. More sulphurous acid should be added if, at any time, the water in the flask no longer has a strong odour of that acid. It is not necessary to boil when less than 250 c.c. of the water is used. If the sample contains more than 0·5 part of nitrogen as nitrates and nitrites, fill up the dish after the water has been evaporated to dryness, or nearly so, with pure distilled water containing 10 per cent. of a saturated solution of sulphurous acid, and again evaporate to dryness. If the nitrogen as nitrates exceeds 1 part, evaporate on the residue 250 c.c. of such an acid mixture; if 2 parts, half a litre; and if 5 parts, a litre. A proportional volume should be used if the quantity of the sample which has been evaporated was other than a litre.

With sewage, and similar liquids which do not contain nitrates or nitrites, it is better to use metaphosphoric acid in place of sulphurous acid, as the loss of ammonia is then less. Add to the liquid to be evaporated 10 c.c. of a solution made by dissolving 100 grams. of sticks of glacial metaphosphoric acid in a litre of water; and in order to give the residue a less tenacious character than it would otherwise possess, add also about half a gram. of calcic phosphate, prepared by precipitating common phosphate of soda by calcic chloride, washing the precipitate by decantation, drying, and heating it to redness.

The quantity of carbon and nitrogen present in a water residue thus obtained would, in most cases, be so extremely small as to render the ordinary process of ultimate organic analysis inapplicable; but by conducting the combustion in a vacuum obtained by the Sprengel-pump this difficulty is completely overcome.

A piece of narrow combustion tube, about 10 m.m. in internal diameter, and 430 m.m. in length, is first thoroughly cleansed inside, washed with distilled water, dried, and sealed at one end by the blowpipe.

To effect the combustion of the organic matter in the residue, it is mixed with cupric oxide, and this requires special preparation. That which has been prepared by igniting cupric nitrate cannot be used, as, no matter how long and intense the ignition has been, it will still give off carbonic anhydride and nitrogen when heated *in vacuo*. It is, therefore, necessary to employ oxide which has been prepared by oxidising metallic copper sheet or wire, in a muffle, or on the hearth of a reverberatory furnace, with free access of air. It is desirable before use to reheat it in a large iron tube placed in the combustion furnace, and maintained at a red heat for about two hours. As soon as it is sufficiently cooled, but while still very warm, it should be removed from the iron tube, the finer portions sifted out by means of a sieve of clean copper gauze, and both fine and coarse oxide preserved in well-stoppered bottles. The oxide may be used repeatedly, the tube being broken after the combustion and the oxide refurnaced, rejecting that which was mixed with the residue.

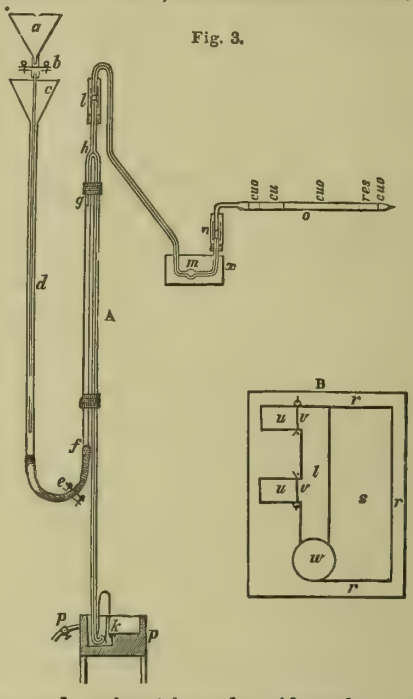
The solid residue left in the glass dish on evaporation of the water is transferred to a combustion tube in the following manner. Into the closed end of the tube introduce enough coarse oxide of copper to fill about 30 m.m. of the length of the tube, then pour into the residue in the glass dish a little of the fine oxide, and with a small, very elastic steel spatula, carefully detach the residue from the glass and mix it with the oxide, rubbing the latter against the sides of the dish to assist in detaching the residue. When the contents of the dish are well mixed together they are transferred to the tube by the usual scooping motion, and the last portions by the help of a piece of highly glazed card, or of smooth, clean platinum foil. The dish is then twice rinsed with a little more fine oxide, which is carefully rubbed round with the spatula each time, and then transferred to the tube. During this operation the dish should stand on a piece of clean glazed paper, and any particles which may fall on to the paper are also put into the tube. The mixture of residue with fine oxide should occupy about 100 m.m. of the length of the tube, which is then to be filled up

with coarse oxide to a distance of about 270 m.m. from the closed end. Next introduce a plug of metallic copper gauze, made by tightly rolling a slip of fine copper gauze (free from zinc), 80 m.m. wide, round a copper wire, and covering the compact cylinder thus formed with an outer case of rather thin sheet copper, the edges being made to meet without overlapping. The diameter when finished should be such that it fits easily into the combustion tube. A number of these cylinders are put into a piece of combustion tube, heated to redness in the furnace, oxidised superficially by passing a current of air through the tube, and the oxide thus formed then reduced to the metallic state by substituting dry hydrogen for the air, the current of hydrogen being continued during the cooling of the tube. The copper cylinders should be preserved in a stoppered bottle. They may be used two or three times, and should then be again heated in a current of hydrogen, and so on.

After inserting the copper plug, introduce about 20 m.m. in length of coarse oxide in order to oxidise any traces of carbonic oxide which may have been produced by impurities in the copper gauze. Draw off the open end of the tube before the blow-pipe, to form a neck about 100 m.m. in length and 4 m.m. in diameter; smooth the end where cut off by heating it in the blow-pipe flame, and bend the neck at right angles. It is then placed in the combustion furnace, care being taken so to arrange it that the whole of the contents of the tube can be, when desired, heated to redness.

To exhaust the tube in the first instance, and afterwards to remove and collect the gaseous products of the combustion, the Sprengel mercury pump is employed, a convenient form of which is shown in Fig. 3. The glass funnel, *a*, is filled with mercury, and is connected by means of a short caoutchouc tube, on which is a screw, *e*, pinch-cock, *b*, with a long narrow tube extending nearly to the bottom of the outer tube, *d*, which is about 900 m.m. in length and about 10 m.m. in internal diameter, and is secured in the neck of the glass funnel, *c*, by means of plaster of Paris. This supply tube is connected by means of a longer piece of caoutchouc, which, to withstand the internal pressure of mercury, must be covered closely with a strong sheath of canvas or tape, with the mercury pump proper. A screw pinch-cock on the caoutchouc tube controls the flow of mercury through it. The ascending limb of the pump, *f g*, consists of a common narrow glass tube, and is about 600 m.m. in length. At *g* it is fused on to a piece of thick tube with a bore of 1 m.m. and 1500 m.m. in length, which is bent on itself at *h*, whilst at the open end, *k*, it is curved sharply upwards. At *h* a short piece of tube, similar to *f g*, is fused in, open at the top and carrying on it a wider glycerin tube, *l*, which slides up and down on the narrow tube by means of a caoutchouc stopper. At *l* the bent connecting tube, *l m n*, is attached by a short caoutchouc tube, so that the wider tube filled with glycerin can be pushed up over the joint, which is thus entirely immersed in glycerin, and leakage of air inwards effectually prevented. The connecting tube has a bore of 1 m.m., and has a small bulb blown on

Fig. 3.



it at *m*, and carries at its end a wider tube, *n*, which can be filled with water to cover the joint by which the combustion tube, *o*, is attached. Glycerin is used in *l*, as that joint is seldom detached, and is introduced merely to give flexibility to the apparatus. The two limbs of the tube, *f g*, are firmly lashed together at two points, the tubes being there covered by short pieces of caoutchouc tube to prevent fracture. The funnels, *a* and *c*, rest in ring supports, but the pump, *f h k*, rests entirely on the end *k*; the upper part being held in a forked guide in which it is free to move towards or from the combustion furnace.

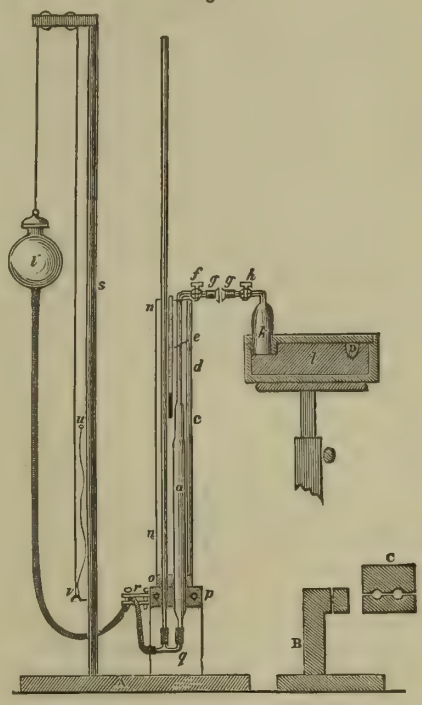
The pump may stand in a porcelain or wooden mercury trough of any convenient form. When two pumps are employed a convenient form of trough is that shown at B; where *t* is a deep channel having two recesses, *u u*, communicating with it to receive the pumps, the recurved ends of these being towards the channel, *t*. The test tubes in which the gases are collected are filled with mercury in the channel, *t*, and are then inverted over the ends of the pumps, and are kept upright in the recesses by little wire gates, *v v*, across the entrances. At *w* is a well 90 m.m. deep and 42 m.m. in diameter; the channel, *t*, is 75 m.m. deep and 25 m.m. wide; the recesses are 40 m.m. long, 25 m.m. wide, and 75 m.m. deep; the shelf, *s*, is 50 m.m. deep. The whole is cut out of a solid piece of mahogany and stands on four short legs, so that mercury can readily be drawn off from it to the level of the shelf, *s*, by means of the pinch-cock, *b*.

In the furnace the tube rests in a trough of sheet

iron on a bed of fine asbestos, in order to avoid local irregularities of heating. As soon as the tube is properly connected with the pump by the joint at *n*, the gas burners of the front part of the furnace are lighted, so as to heat to redness the whole of the plug of metallic copper and part of the oxide, care being taken that the part of the tube containing the residue is not heated. A screen of sheet iron should be placed in the furnace to protect this part. At the same time the pump is put in action, the flow of mercury being regulated by the pinch-cocks, *b* and *e*, so that it shall fall in the tube, *h k*, in a slow steady stream of well formed pistons. During this exhaustion a small trough, *x*, is filled with hot water, so as to cover the bulb, *m*, and thus expel any moisture left there in a previous operation. As the exhaustion proceeds the mercury will fall more and more rapidly in *h k*, until, when a vacuum is attained, each pellet falls with a sharp clicking sound. When this occurs, and the front part of the tube is at a red heat, the pump is stopped, a test tube carefully filled with mercury inverted over the end of *h k*, the iron screen taken from the furnace, and the combustion proceeded with in the usual manner; care being taken that, when the organic matter begins to burn, the operation proceeds very slowly until the vacuum is considerably impaired, otherwise traces of carbonic oxide may escape oxidation. The hot water in *x* should be removed, and cold substituted, to condense water produced in the combustion. The combustion will occupy from fifty to sixty minutes; as soon as the whole of the tube has been heated to redness the gas is extinguished and the pump again worked until the whole of the gases produced have been removed to the test tube, and the combustion tube is again vacuous. This mixture of gases contains carbonic anhydride, nitric oxide, nitrogen, and (very rarely) carbonic oxide; and their separation and determination presents no difficulty, and in the apparatus presently to be described occupies some twenty minutes only.

This apparatus is shown in outline in Fig. 4, where *a c d* is a measuring tube, of which the cylindrical portion, *a*, is 370 m.m. long and 18 m.m. in internal diameter; *c* 40 m.m. long and 7 m.m. in diameter; and *d* 175 m.m. long and 2·5 m.m. in diameter. Allowing for the tapering parts where *a*, *c*, and *d* are joined, and for the narrow part at the bottom, the entire length from the rectangular bend at the top is 650 m.m. The upper end terminates in a glass tube with fine capillary bore and stop-cock, *f*. The pressure tube, *b*, is about 1·2 metre long and about 6 m.m. in internal diameter. At the bottom it is drawn off like *a* to about 5 m.m. external diameter. Both *a* and *b* are graduated in millimetres, the zeros being about 100 m.m. from the bottom; the graduations in *a* need, however, only mark every tenth millimetre, except at the top of *d*, where the last 10 m.m. should be marked with single millimetres. Both *a* and *b* are fitted into a glass water jacket, *n n*, by means of a caoutchouc plug, *o*, through which they pass water tight. Below this they are firmly held by a wooden clamp, *p* (shown in end elevation and plan at B C), the two

Fig. 4.



parts of which are drawn tightly together by two common screws, the upright being firmly secured to the large base, A. To protect the tubes from fracture, they are sheathed in short pieces of caoutchouc tube where they pass through the clamp. Care must be taken that the semi-cylindrical grooves cut in the clamp for the reception of the tubes are of proper size and perpendicular to the base, A, so that the tubes themselves may be exactly perpendicular and parallel. When firmly clamped, and the plug, *o*, tightly fitted, no other support will be required either for the tubes or water-jacket. Below the clamp the lower ends of *a* and *b* are carefully joined by caoutchouc connectors, covered with strong tape, and tightly bound with wire to the vertical limbs of the connecting piece, *q*; and to the horizontal leg of this is attached a caoutchouc tube about 1·5 metres long, covered with tape, and which, passing through the double-screw clamp, *r*, one bar of which is screwed into the side of the clamp, *p*, communicates with the reservoir, *t*. This is hung from a kind of derrick, *s*, by means of a cord passing over two grooved pulleys. The cord is arranged so that when suspended from the eye, *u*, the bottom of *t* is level with the bottom of the clamp, *p*; and a loop is made on the cord by which it may be attached to the hook, *v*, as shown in the figure, and the bottom of *t* should then be about 100 m.m. above *f*. A stout caoutchouc band fitted round *t* is a useful defence in case of an accidental blow against the rod, *s*. A thermometer, graduated into fifths or tenths of a degree Centigrade, suspended in the water-jacket,

$n\,n$, indicates the temperature of the water, and hence of the gas being measured. Chemical agents are applied to the gas under examination in the laboratory vessel, k, which is a glass cylinder, about 100 m.m. high and 35 to 40 m.m. in diameter, open at bottom and terminating at top in a piece of glass tube with a capillary bore and stop-cock, h, similar to that on the measuring tube. Each of these narrow tubes carries, secured by cement at its end, a steel cap, shown in section at B, Fig. 5, the polished faces of which can be tightly pressed together by means of the clamp, A, and thus a capillary communication is established between the measuring tube and the laboratory vessel, nevertheless permitting of the ready removal of the latter when required for cleansing, and its equally ready replacement. The laboratory vessel stands in a mercury

Fig. 5.

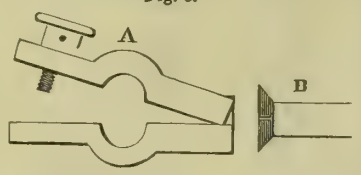
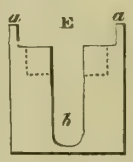


Fig. 6.



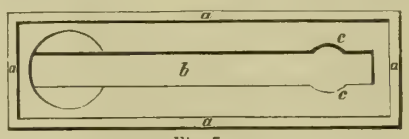


Fig. 7.

trough, shown in longitudinal section in Fig. 4, l; in transverse section in Fig. 6; and in plan in Fig. 7. It is 265 m.m. long, 80 m.m. broad, and 90 m.m. deep outside. It must be cut out of a single block of mahogany. The channel, b, is 230 m.m. long, 26 m.m. broad, and 65 m.m. deep. At one end it has a kind of well 45 m.m. in diameter, and 20 m.m. deep from the edge of b; and near the other end are two small recesses, one on each side, shown at $c\,c$, Fig. 7, for the admission of a small capsule or beaker, used in transferring test tubes containing gas to be examined. This trough must be adjusted at such a level, with regard to the measuring tube, that when the laboratory vessel is in its place the two steel caps exactly face each other, and can be clamped together without straining either of the tubes.

As, owing to the difference between the diameters of the pressure tube of the measuring apparatus and the various parts of the measuring tube, capillary action will have considerable effect on the level of mercury in them, this must be ascertained by noticing the point at which the surface of the mercury stands in the pressure tube, and successively in each of the three parts of the measuring tube when both are freely open to the air above; and this correction must in using the apparatus always be added to or deducted from the observed pressure, according as the mercury with the tubes thus open stands in the measuring tube above or below that in the pressure tube. This, and all observations with the gas apparatus, should be made through a telescope properly levelled. The correction for capillarity will also include any that may be necessary for any small difference of level between the zeros of the two graduated tubes; and it should occasionally be re-determined in case any change in this respect should have taken place.

Before the apparatus can be used, its capacity at each graduation must be accurately ascertained. It is first filled with mercury, and then distilled water is introduced into the measuring tube (either by means of a funnel attached by a caoutchouc tube to the steel cap, or by injecting water by a pipette into the laboratory vessel whilst that is attached to the measuring tube), until the level of the mercury is below the zero of the graduation. It is allowed to stand a few minutes until the temperature of the water in the tube corresponds with that of the water in the jacket. The reservoir being raised, the stop-cock, f, is opened cautiously, and water allowed to escape slowly, until the top of the surface of the mercury in the tube just corresponds with the zero of the scale. The face of the steel cap should be greased so that the drops of water fall off without adhering. A light glass flask carefully weighed is then placed so as to receive the drops which fall from the steel cap, and the temperature being noted, the water is allowed to drop gently into the flask until the mercury stands at 100 m.m., when the cock is again closed, the flask removed and weighed, and the weight of water collected ascertained. This is repeated until the whole of the water has been expelled from the tube and weighed. Care should be taken, however, that the weight is noted at the highest point on a, at which the tube has remained unaltered in fusing on the part c, and again at the lowest and highest graduations on the undeformed parts of c and d. From these weighings, which should be made in duplicate, a table should be calculated giving the capacity of the tube from every tenth millimetre to the top. If the tube is irregular in diameter, observations should be made at shorter intervals than 100 m.m. The volume of the water, thus weighed, should be calculated by means of the following table:—

THE WEIGHT OF 1000 C.C. OF WATER AT $t°$ C. WEIGHED WITH BRASS WEIGHTS IN AIR OF $t°$ C. IS EQUAL TO 1000—x GRAMS.

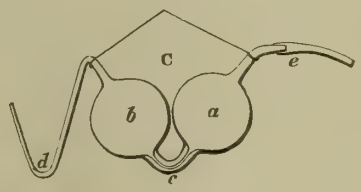
$t°$	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
x,.....	1·25	1·20	1·15	1·13	1·12	1·12	1·14	1·16	1·21	1·27	1·34	1·43	1·52	1·63	1·76	1·89
$t°$	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.	29.	30.	
x,.....	2·04	2·20	2·37	2·55	2·74	2·95	3·17	3·39	3·63	3·88	4·13	4·39	4·67	4·94	5·24	

It will save some trouble in practice if this table consists of the logarithms of the numbers representing the capacity of the tube in c.c.'s rather than of the natural numbers. It is sufficient to take the logarithms to five decimal places.

To use the apparatus, pour mercury into the reservoir, *t*, and allow it to pass the pinch-cock, *r*, until it has entirely filled the measuring tube and drips from the capillary tube at *g*. The cock at *f* is then closed, and the laboratory vessel being placed in position is filled with mercury, either by exhausting the air through *h*, or better, by putting one end of a short piece of caoutchouc tube in it before placing it in position, and then drawing air through the tube like an inverted siphon. The caoutchouc can then be removed, and any remaining bubbles drawn out through *h*. Both being filled completely with mercury, the faces of the steel caps are greased with a little resin cerate, softened if necessary by the addition of a little oil; they are carefully placed in contact and firmly clamped together. On opening the cocks, *f* and *h*, mercury should pass freely through the capillary communication, and on closing *h* and lowering *t* to its lowest position, *r* being still open, no leakage should take place into *a c d*. All being ready, transfer the gas to be examined to the laboratory vessel, and with a small pipette having an almost capillary delivering tube, the end of which is curved upwards, introduce two or three drops of a saturated solution of bichromate of potash. If the solution becomes green, sulphurous acid is present, and must be absorbed by the bichromate, of which more must be added if necessary. The action of liquids on the gas may be much facilitated by gently shaking the mercury trough in which the vessel stands, or rather by making the stand on which the trough is supported vibrate so as to throw the liquid up on to the sides of the laboratory vessel, and thus expose a large wet surface. After about five minutes the whole of the sulphurous acid will have been absorbed. During this time, and at any time during which the gas is exposed to the action of a reagent, mercury is allowed to pass slowly into the laboratory vessel by the capillary connection, to mix the gas and remove liquid from the mouth of the capillary tube. Having insured the absence of sulphurous acid, open both stop-cocks, *f* and *h*, lower the reservoir, *t*, and thus drive the gas over into the measuring tube. Close the stop-cock, *h*, as soon as the liquid following the gas is within about 10 m.m. of the stop-cock. Then by raising or lowering the reservoir, *t*, bring the surface of the mercury in the measuring tube to coincide, as seen in the telescope, with a convenient graduation, the capacity of the apparatus down to which is known. The flow of mercury is controlled by the pinch-cock, *r*. This done, observe the position of the mercury in the pressure tube and measuring tube, the temperature of the water in the jacket, and the barometric pressure of the air; reading pressures to a tenth of a millimetre, and the temperature to a tenth of a degree Centigrade. Next, introduce into the laboratory vessel a few drops of a cold saturated solution of caustic potash, and drive the gas back again into the laboratory vessel to absorb CO_2. In about three or five minutes this will be effected, and the gas is returned to the measuring tube and again measured as before, except that it is not necessary to observe the barometer again.

Now add to the contents of the laboratory vessel a few drops of a cold saturated solution of pyrogallic acid, and return the gas upon it. When the quantity of gas is very small, and the vacuum therefore but slightly impaired during the combustion, there is occasionally given off a trace of oxygen, which will be indicated by a dark stain on the sides of the laboratory vessel when the gas encounters the alkaline pyrogallate. If oxygen be present, allow the gas to remain for five minutes to absorb it. The presence of oxygen involves, of course, the loss of any nitric oxide which has also escaped the reducing action of the copper; but this is a very small proportion of an already very small quantity, and therefore is of no moment. If oxygen be not present, add a few bubbles of pure oxygen from a pipette, a very convenient form of which is shown in Fig. 8, where *a* and *b* are two small glass bulbs

Fig. 8.



blown on a piece of glass tube, similar to that used for the Sprengel pump, about 50 m.m. in diameter. The connecting tube is constricted at *c*, so that mercury can only pass very slowly through it; the delivery tube, *d*, is drawn out to a capillary bore. Pure oxygen is obtained by heating dry powdered chlorate of potash in a bulb retort, made by blowing a bulb on a piece of combustion tube, drawing out close to the bulb a very long narrow neck, which after the introduction of the chlorate is bent twice in opposite directions, so as to form a convenient delivery tube, the sharply bent up end of which just dips below the surface of mercury in a mercury trough. The first 60 or 80 c.c. of oxygen being rejected, a sufficient quantity is collected in test tubes, each of which is removed from the trough in a very small beaker, containing enough mercury to effectually confine the oxygen. The first tube should be tested by transferring about 10 c.c. of the gas to another tube, and heating it with alkaline pyrogallate. If only a very small bubble is left unabsorbed, the gas in that and the succeeding tubes may be considered pure, otherwise the second tube is similarly tested, and so on. The oxygen pipette is charged by filling the bulb, *b*, and the tubes, *d* and *c*, with mercury, introducing *d* into a test tube of oxygen, and drawing air from *e*; the gas will then enter *b*. It is necessary to see that *d* is filled with mercury before removing the pipette

after introducing oxygen to the laboratory vessel. As soon as the liquid in the laboratory vessel, when thrown up against the side, runs off without leaving a dark stain on the glass, all the oxygen is known to be absorbed, and the gas is again measured. We have thus three measurements of the gas which may be called A, B, and C. A — B = the CO_2; B — C = the nitric oxide; and C = the nitrogen. The most rapid method of calculating the carbon and nitrogen from these volumes is to assume that all the gas is nitrogen; calculate the weight of each volume on that supposition, and then calculate the quantity of carbon corresponding to the nitrogen, whose volume is A — B. The weight of the carbon is $(A - B)\frac{3}{7}$, and of the nitrogen, $\frac{B-C}{2} + C = \frac{B+C}{2}$. One cubic centimetre of nitrogen at 0° C. and 760 m.m. pressure, weighs 0·0012562 gram., so that the weight of v c.c. of nitrogen at p m.m. pressure, and t° C. is $\frac{0{\cdot}0012562 \times v \times p}{(1 + 0{\cdot}00367\,t)760}$. As the inner surface of the measuring tube is always kept moist with water, the gas when measured is always saturated with aqueous vapour, and the pressure observed must be corrected for this. Table I. gives the elasticity of aqueous vapour in millimetres of mercury for each 0·1° C. from 0° to 30°; and in Table II. is given the logarithm of the value of the expression $\frac{0{\cdot}0012562}{(1 + 0{\cdot}00367\,t)\,760}$ for a similar range of temperature.

TABLE I. — ELASTICITY OF AQUEOUS VAPOUR FOR EACH ONE-TENTH DEGREE CENTIGRADE FROM 0° TO 30° C. (REGNAULT.)

Temperature. Degrees C.	Tension in Millimetres of Mercury.	Temperature. Degrees C.	Tension in Millimetres of Mercury.	Temperature. Degrees C.	Tension in Millimetres of Mercury.	Temperature. Degrees C.	Tension in Millimetres of Mercury.	Temperature. Degrees C.	Tension in Millimetres of Mercury.
0	4·6	6·0	7·0	12·0	10·5	18·0	15·4	24·0	22·2
·1	4·6	·1	7·0	·1	10·5	·1	15·5	·1	22·3
·2	4·7	·2	7·1	·2	10·6	·2	15·6	·2	22·5
·3	4·7	·3	7·1	·3	10·7	·3	15·7	·3	22·6
·4	4·7	·4	7·2	·4	10·7	·4	15·7	·4	22·7
·5	4·8	·5	7·2	·5	10·8	·5	15·8	·5	22·9
·6	4·8	·6	7·3	·6	10·9	·6	15·9	·6	23·0
·7	4·8	·7	7·3	·7	10·9	·7	16·0	·7	23·1
·8	4 9	·8	7·4	·8	11·0	·8	16·1	·8	23·3
·9	4·9	·9	7·4	·9	11·1	·9	16·2	·9	23·4
1·0	4·9	7·0	7·5	13·0	11·2	19·0	16·3	25·0	23·5
·1	5·0	·1	7·5	·1	11·2	·1	16·4	·1	23·7
·2	5·0	·2	7·6	·2	11·3	·2	16·6	·2	23·8
·3	5·0	·3	7·6	·3	11·4	·3	16·7	·3	24·0
·4	5·1	·4	7·7	·4	11·5	·4	16·8	·4	24·1
·5	5·1	·5	7·8	·5	11·5	·5	16·9	·5	24·3
·6	5·2	·6	7·8	·6	11·6	·6	17·0	·6	24·4
·7	5·2	·7	7·9	·7	11·7	·7	17·1	·7	24·6
·8	5·2	·8	7·9	·8	11·8	·8	17·2	·8	24·7
·9	5·3	·9	8·0	·9	11·8	·9	17·3	·9	24·8
2·0	5·3	8·0	8·0	14·0	11·9	20·0	17·4	26·0	25·0
·1	5·3	·1	8·1	·1	12·0	·1	17·5	·1	25·1
·2	5·4	·2	8·1	·2	12·1	·2	17·6	·2	25·3
·3	5·4	·3	8·2	·3	12·1	·3	17·7	·3	25·4
·4	5·5	·4	8·2	·4	12·2	·4	17·8	·4	25·6
·5	5·5	·5	8·3	·5	12·3	·5	17·9	·5	25·7
·6	5·5	·6	8·3	·6	12·4	·6	18·0	·6	25·9
·7	5·6	·7	8·4	·7	12·5	·7	18·2	·7	26·0
·8	5·6	·8	8·5	·8	12·5	·8	18·3	·8	26·2
·9	5·6	·9	8·5	·9	12·6	·9	18·4	·9	26·4
3·0	5·7	9·0	8·6	15·0	12·7	21·0	18·5	27·0	26·5
·1	5·7	·1	8·6	·1	12·8	·1	18·6	·1	26·7
·2	5·8	·2	8·7	·2	12·9	·2	18·7	·2	26·8
·3	5·8	·3	8·7	·3	12·9	·3	18·8	·3	27·0
·4	5·8	·4	8·8	·4	13·0	·4	19·0	·4	27·1
·5	5·9	·5	8·9	·5	13·1	·5	19·1	·5	27·3
·6	5·9	·6	8·9	·6	13·2	·6	19·2	·6	27·5
·7	6·0	·7	9·0	·7	13·3	·7	19·3	·7	27·6
·8	6·0	·8	9·0	·8	13·4	·8	19·4	·8	27·8
·9	6·1	·9	9·1	·9	13·5	·9	19·5	·9	27·9
4·0	6·1	10·0	9·2	16·0	13·5	22·0	19·7	28·0	28·1
·1	6·1	·1	9·2	·1	13·6	·1	19·8	·1	28·3
·2	6·2	·2	9·3	·2	13·7	·2	19·9	·2	28·4
·3	6·2	·3	9·3	·3	13·8	·3	20·0	·3	28·6
·4	6·3	·4	9·4	·4	13·9	·4	20·1	·4	28·8
·5	6·3	·5	9·5	·5	14·0	·5	20·3	·5	28·9
·6	6·4	·6	9·5	·6	14·1	·6	20·4	·6	29·1
·7	6·4	·7	9·6	·7	14·2	·7	20·5	·7	29·3
·8	6·4	·8	9·7	·8	14·2	·8	20·6	·8	29·4
·9	6·5	·9	9·7	·9	14·3	·9	20·8	·9	29·6
5·0	6·5	11·0	9·8	17·0	14·4	23·0	20·9	29·0	29·8
·1	6·6	·1	9·9	·1	14·5	·1	21·0	·1	30·0
·2	6·6	·2	9·9	·2	14·6	·2	21·1	·2	30·1
·3	6·7	·3	10·0	·3	14·7	·3	21·3	·3	30·3
·4	6·7	·4	10·1	·4	14·8	·4	21·4	·4	30·5
·5	6·8	·5	10·1	·5	14·9	·5	21·5	·5	30·7
·6	6·8	·6	10·2	·6	15·0	·6	21·7	·6	30·8
·7	6·9	·7	10·3	·7	15·1	·7	21·8	·7	31·0
·8	6·9	·8	10·3	·8	15·2	·8	21·9	·8	31·2
·9	7·0	·9	10·4	·9	15·3	·9	22·1	·9	31·4

TABLE II.—REDUCTION OF CUBIC CENTIMETRES OF NITROGEN TO GRAMS.

Log. $\frac{0{\cdot}0012562}{(1 + 0{\cdot}00367t)760}$ for each tenth of a degree from 0° to 30° C.

t° C.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0°	$\bar{6}$·21824	808	793	777	761	745	729	713	697	681
1	665	649	633	617	601	586	570	554	538	522
2	507	491	475	459	443	427	412	396	380	364
3	349	333	318	302	286	270	255	239	223	208
4	192	177	161	145	130	114	098	083	067	051
5	035	020	004	*989	*973	*957	*942	*926	*911	*895
6	$\bar{6}$·20879	864	848	833	817	801	786	770	755	739
7	723	708	692	676	661	645	629	614	598	583
8	567	552	536	521	505	490	474	459	443	428
9	413	397	382	366	351	335	320	304	289	274
10	259	244	228	213	198	182	167	151	136	121
11	106	090	075	060	045	029	014	*999	*984	*969
12	$\bar{6}$·19953	938	923	907	892	877	862	846	831	816
13	800	785	770	755	740	724	709	694	679	664
14	648	633	618	603	588	573	558	543	528	513
15	497	482	467	452	437	422	407	392	377	362
16	346	331	316	301	286	271	256	241	226	211
17	196	181	166	151	136	121	106	091	076	061
18	046	031	016	001	*986	*971	*956	*941	*926	*911
19	$\bar{6}$·18897	882	867	852	837	822	807	792	777	762
20	748	733	718	703	688	673	659	644	629	614
21	600	585	570	555	540	526	511	496	481	466
22	452	437	422	408	393	378	363	349	334	319
23	305	290	275	261	246	231	216	202	187	172
24	158	143	128	114	099	084	070	055	041	026
25	012	*997	*982	*968	*953	*938	*924	*909	*895	*880
26	$\bar{6}$·17866	851	837	822	808	793	779	764	750	735
27	721	706	692	677	663	648	634	619	605	590
28	576	561	547	532	518	503	489	475	460	446
29	432	417	403	388	374	360	345	331	316	302

An example will best show the exact method:—

	A. Total.	B. Nitrogen and Nitric Oxide.	C. Nitrogen.
Volume of gas, ...	c.c. 6·911	c.c. 0·8649	c.c. 0·8649
Temperature, ...	Degrees. 18·1	Degrees. 18·1	Degrees. 18·1
Height of mercury in measuring tube, ...	m.m. 320·0	m.m. 380·0	m.m. 380·0
Height of mercury in pressure tube, ...	144·8	352·6	317·6
Difference, ...	175·2	27·4	62·4

	A. Total.	B. Nitrogen and Nitric Oxide.	C. Nitrogen.
Difference,.....	175·2	27·4	62·4
Add tension of aqueous vapour,.....	15·5	15·5	15·5
	190·7		
Deduct or add correction for capillarity,..	− 0·9	+ 2·2	+ 2·2
	189·8	45·1	80·1
Deduct these numbers from height of barometer,.....	763·0	763·0	763·0
	189·8	45·1	80·1
Tension of dry gas,.....	573·2	717·9	682·9
Log. of volume of gas,..	0·83954	$\bar{1}$·93699	$\bar{1}$·93699
" $\frac{0{\cdot}0012562}{(1+0{\cdot}00367t)760}$	$\bar{6}$·19031	$\bar{6}$·19031	$\bar{6}$·19031
" tension of dry gas,	$\bar{2}$·75831	2·85606	2·83436
" weight of gas calculated as nitrogen, =	$\bar{3}$·78816	$\bar{4}$·98336	$\bar{4}$·96166
	0·0061399	0·0009624	0·0009155

$$A - B = 0{\cdot}0051775$$

$$\div 7 \overline{)\ 0{\cdot}0155325}$$

Weight of carbon, ·00222

$$\frac{B + C}{2} = \frac{0{\cdot}0018779}{2} = 0{\cdot}00094 = \text{weight of nitrogen.}$$

In order to correct for the unavoidable impurities of reagents and contamination acquired in transferring from one vessel to another, and during evaporation, &c., each operator should make several blank experiments to ascertain the "personal error" of himself and his laboratory. In these a litre of purified distilled water should be evaporated with the usual quantities of sulphurous acid and ferrous chloride, with the addition of about 0·1 gram. of freshly ignited sodic chloride, this last being intended to give bulk to the residue, and thus facilitate its removal from the dish. The combustion and gas analysis should be made as usual, and the average amounts of carbon and nitrogen thus ascertained deducted from the results of all analyses. This correction, which will be found to be very constant, will amount, perhaps, to about 0·0001 gram. of carbon, and 0·00005 gram. of nitrogen.

Although the loss of ammonia during evaporation is extremely small, still, when the amount present is large, it is necessary to apply a correction for this loss, which appears to be very constant, as shown in Table III. The amount of nitrogen corresponding to the quantity of ammonia present in the water should be added to the quantity of nitrogen found by combustion. The quantities in the Table refer to parts per 100,000. In the analysis of sewage, where metaphosphoric acid has been used, the correction should be taken from Table IV.

TABLE III. — PARTS IN 100,000. LOSS OF NITROGEN BY EVAPORATION OF NH_3 WITH SULPHUROUS ACID.

NH_3	Loss of N.	NH_3	Loss of N.	NH_3	Loss of N.	NH_3	Loss of N.	NH_3	Loss of N.
6·0	1·727	4·6	1·372	3·2	·819	1·8	·321	·4	·062
5·9	1·707	4·5	1·332	3·1	·779	1·7	·309	·3	·047
5·8	1·688	4·4	1·293	3·0	·740	1·6	·297	·2	·032
5·7	1·668	4·3	1·253	2·9	·700	1·5	·285	·1	·017
5·6	1·648	4·2	1·214	2·8	·661	1·4	·274	·09	·014
5·5	1·628	4·1	1·174	2·7	·621	1·3	·262	·08	·013
5·4	1·609	4·0	1·135	2·6	·582	1·2	·250	·07	·012
5·3	1·589	3·9	1·095	2·5	·542	1·1	·238	·06	·010
5·2	1·569	3·8	1·056	2·4	·503	1·0	·226	·05	·009
5·1	1·549	3·7	1·016	2·3	·463	·9	·196	·04	·007
5·0	1·530	3·6	·977	2·2	·424	·8	·166	·03	·006
4·9	1·490	3·5	·937	2·1	·384	·7	·136	·02	·004
4·8	1·451	3·4	·898	2·0	·345	·6	·106	·01	·003
4·7	1·411	3·3	·858	1·9	·333	·5	·077	·009	·001

TABLE IV. — LOSS OF NITROGEN BY EVAPORATION OF NH_3 WITH METAPHOSPHORIC ACID.

Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N. per 100,000.
c.c.			c.c.			c.c.		
100	10·0	·483	100	6·3	·354	100	2·6	·195
100	9·9	·480	100	6·2	·351	100	2·5	·190
100	9·8	·476	100	6·1	·348	100	2·4	·184
100	9·7	·473	100	6·0	·345	100	2·3	·179
100	9·6	·469	100	5·9	·341	100	2·2	·174
100	9·5	·466	100	5·8	·337	100	2·1	·169
100	9·4	·462	100	5·7	·333	100	2·0	·164
100	9·3	·459	100	5·6	·330	100	1·9	·158
100	9·2	·455	100	5·5	·326	100	1·8	·153
100	9·1	·452	100	5·4	·322	100	1·7	·148
100	9·0	·448	100	5·3	·318	100	1·6	·143
100	8·9	·445	100	5·2	·314	100	1·5	·137
100	8·8	·441	100	5·1	·310	100	1·4	·132
100	8·7	·438	100	5·0	·306	100	1·3	·127
100	8·6	·434	100	4·9	·302	100	1·2	·122
100	8·5	·431	100	4·8	·298	100	1·1	·117
100	8·4	·428	100	4·7	·294	100	1·0	·112
100	8·3	·424	100	4·6	·291	250	0·9	·096
100	8·2	·421	100	4·5	·287	250	0·8	·080
100	8·1	·417	100	4·4	·283	250	0·7	·070
100	8·0	·414	100	4·3	·279	250	0·6	·060
100	7·9	·410	100	4·2	·275	500	0·5	·050
100	7·8	·407	100	4·1	·271	500	0·4	·040
100	7·7	·403	100	4·0	·267	500	0·3	·030
100	7·6	·400	100	3·9	·262	1000	0·2	·020
100	7·5	·396	100	3·8	·257	1000	0·1	·010
100	7·4	·393	100	3·7	·252	1000	0·09	·009
100	7·3	·389	100	3·6	·247	1000	0·08	·008
100	7·2	·386	100	3·5	·242	1000	0·07	·007
100	7·1	·382	100	3·4	·236	1000	0·06	·006
100	7·0	·379	100	3·3	·231	1000	0·05	·005
100	6·9	·375	100	3·2	·226	1000	0·04	·004
100	6·8	·372	100	3·1	·221	1000	0·03	·003
100	6·7	·368	100	3·0	·216	1000	0·02	·002
100	6·6	·365	100	2·9	·211	1000	0·01	·001
100	6·5	·361	100	2·8	·205			
100	6·4	·358	100	2·7	·200			

The nitrogen thus obtained includes that present in the water as a constituent of organic matter (organic nitrogen), and that in the form of ammonia. The latter, the determination of which will next be considered, being deducted, the remainder is the amount of the organic nitrogen in the water.

To the organic carbon and nitrogen we must look to form an opinion on the character of the sample, as regards actual organic contamination. It is not

desirable that water which is to be used for drinking and cooking, such as the water supply of a town, should contain in 100,000 parts more than 0·2 part and 0·02 part of these constituents respectively. Unpolluted upland surface waters contain, when tolerably free from peaty matter, from 0·1 to 0·2 part of carbon. and from 0·01 to 0·03 part of nitrogen. Water which has drained from a peat district is usually more or less brown in colour, and the carbon is increased in a larger ratio than the nitrogen. Water from cultivated surfaces contains a larger proportion of organic matter, the organic carbon being usually from 0·25 to 0·3 part, and the organic nitrogen from 0·04 to 0·05. In shallow well waters the variation is excessive, and no range can be stated. In deep well waters the organic matter is generally low, being usually about 0·06 of carbon and 0·02 of nitrogen, or less. Spring waters much resemble deep well waters. In both the character of the water is very constant, the conditions being practically unaffected by surface changes; whilst in the preceding class of shallow wells the reverse is the case, meteorological variations and the incessant changes of surface pollution at once affecting the water of the well. This renders all such wells dangerous as sources of water supply, as there is no security that, even if the water should be pure to-day, it may not be fatally polluted to-morrow. The oxidising action which effectually destroyed a certain quantity of noxious matter may be in great part suspended, or may be incapable of destroying a larger quantity; moreover, although dead organic matter may be oxidised, we do not know that the same may be expected in regard to the specific poisons of disease, which are organized and living. Average sewage contains about 4 parts of organic carbon and 2 parts of organic nitrogen, but the range is very great.

The *ratio* of the organic carbon to the organic nitrogen is important, being as a rule high when the source of the organic matter is vegetable, and low when it is animal. When organic matter of vegetable origin is oxidised, it loses carbon more rapidly than nitrogen, so that the ratio is gradually reduced; when of animal origin, it loses nitrogen more rapidly than carbon, and the ratio therefore increases. In peaty waters it amounts to about 12 on the average (*i.e.* $\frac{C}{N} = 12$), but may reach 20 or even a larger amount; upland surface water containing but a small proportion of peat gives a ratio of 6 to 12; water from cultivated areas about 6; shallow wells about 4, with a very wide range; deep wells and springs about 4, with a much narrower range; sea-water about 1·7; sewage about 1 to 3, with an average of 2.

Ammonia.—For the estimation of ammonia Nessler's solution and a standard ammonic chloride solution are required. For the former, dissolve 62·5 grams. of potassic iodide in 250 c.c. of distilled water, and add gradually cold saturated solution of corrosive sublimate, until the red precipitate formed on each addition just ceases to be redissolved on stirring. Then dissolve 150 grams. of solid potassic hydrate in 150 c.c. of water, allow the solution to cool, add it to the first solution, make up with distilled water to one litre, mix well, and allow to stand. A brown precipitate is deposited, the clear solution being of a pale greenish yellow colour. As soon as it is perfectly clear it is ready for use.

The standard solution of ammonic chloride is made by dissolving 1·5735 gram. of the pure dry salt in water, and making up with water to one litre. This solution should be diluted to ten times its volume for use; 1 c.c. will then correspond to 0·00005 gram. of ammonia (NH_3).

The estimation depends on the formation of a yellow or brownish coloration when Nessler's solution is added to a highly dilute ammoniacal solution; the intensity of the colour being estimated by comparison with that produced by a known quantity of ammonia. Add to about 50 c.c. of the water to be examined, in a white glass cylinder about 150 m.m. high and of about 70 c.c. capacity, about 1 c.c. of Nessler's solution, stir with a clean glass rod, and allow to stand for five minutes. If the colour then produced, as seen standing on a white surface, is not deeper than that developed in a similar cylinder in which 0·1 c.c. of the standard ammonic chloride has been diluted with 50 c.c. of water free from ammonia and similarly treated with Nessler's solution, half a litre of the water should be taken for the determination. Should the tint be deeper, less can be taken; but it is not desirable to employ less than 20 c.c. Distilled water, as ordinarily used, is occasionally free from ammonia; but to obtain it as required above, it is generally necessary to rectify it over freshly ignited sodic carbonate, of which sufficient should be added to render it distinctly alkaline. It is then distilled until, on testing the distillate with Nessler's solution as above, no trace of yellow is observed after standing for five minutes. The distillate which subsequently passes over is preserved as "water free from ammonia." The distillation must not be continued to dryness.

If the sample is to be filtered and contains but little ammonia. the *filter paper* must not yield ammonia. If it is found to do so it must be *steeped* for a day or two in water free from ammonia, then transferred while wet direct to the funnel, and the first portion of the filtrate rejected. *Washing* with water, even repeated, is usually insufficient. Unless the sample is very turbid it is not usually necessary to filter it for the estimation of ammonia, although it is to be filtered for those of organic carbon and nitrogen and total solid matters.

A large glass tubulated retort should be used, connected by a short piece of caoutchouc tube with the glass inner tube of a Liebig's condenser. To insure that the retort and condenser are free from ammonia, it is desirable to distil a little common or distilled water with a little sodic carbonate until the distillate is free from ammonia. In making a series of estimations on the same day it is only necessary to do this at the beginning of the series, provided

that each distillation is continued until ammonia ceases to come over. The residue is removed to make way for another estimation by means of a clean glass siphon.

The retort being free from ammonia, the measured quantity of the water is introduced, together with about 1 gram. of recently ignited sodic carbonate, and, if necessary, enough water free from ammonia to make up the volume to about 400 c.c., and the distillation is rapidly proceeded with; the distillate being collected in successive portions of about 50 c.c. each in small glass cylinders previously described. It is best to begin by examining the *second* of these as soon as it is collected; add to it about 1 c.c. of Nessler's solution, stir, and allow it to stand for five minutes. Then observe the colour produced, as seen standing on a white surface, and measure from a narrow burette into a similar cylinder a quantity of standard ammonic chloride which you consider will give, when tested, an equal depth of colour. Add to this about 50 c.c. of water free from ammonia and then 1 c.c. of Nessler's solution, and allow it also to stand for five minutes. If the contents of the two cylinders display the same tint, they contain equal quantities of ammonia; but if not, fresh trial cylinders with a greater or less quantity of ammonia must be prepared until equality is gained. Ammonia solution must not be added *after* the Nessler's solution, or a precipitate will be produced.

Nessler's solution may be added to the second and subsequent fractions of distillate as soon as each is distilled over, and when one is obtained free from ammonia the distillation may be stopped. If the ammonia in the second fraction does not exceed that in 0·4 c.c. of the standard solution, Nessler's solution may be added to the first fraction, and the ammonia in it estimated as above; but if it exceeds that, the first fraction should be measured and an aliquot part taken and diluted to about 50 c.c. with water free from ammonia, and the ammonia determined in this part, as the undiluted fractions would probably give a colour too dark for convenient estimation. When the estimation is thus made in a part it is as well to take another portion and a fresh trial cylinder, adding the Nessler's solution to both at the same time, so that the tints may be compared when they have been standing for the same length of time. If it is known that a large quantity of ammonia is present, time is saved by at once taking as a first fraction about 100 c.c. and diluting a small measured part of this. The volumes of standard ammonic chloride solution corresponding to the various fractions are added together; and if 500 c.c. of the sample were used, the total number of c.c. of the standard solution divided by 100 will express the ammonia (NH_3) present in parts per 100,000.

The ammonia in water is not always of animal origin. In upland waters the average is about 0·002 part per 100,000; in that from cultivated areas about 0·005, with a considerable range; in water from shallow wells all proportions from *nil* to 2·5 parts have been noticed; in deep well waters the average is about 0·001 part, but sometimes in excellent samples amounting to 0·1 part, or even somewhat more; in spring waters the average is only 0·001. Sewage usually contains from 2 to 6 parts, with an average of about 5. The occurrence of a considerable quantity of ammonia usually coincides with much organic matter and deficient oxidation; that found in water from some very deep wells probably results from decomposition of nitrates.

Nitrogen as Nitrates and Nitrites.—This is determined by a modification of a process devised by Walter Crum for the refraction of nitre. The residue from the determination of the total solid matters is treated with 20 to 30 c.c. of hot distilled water, and when the whole has been well wetted with the water, enough of a saturated solution of sulphate of silver is added to precipitate the whole of the chlorine present, and the dish is then heated on a steam bath for some minutes. The sulphate, which is but sparingly soluble, is prepared by acting upon well-washed carbonate of silver with a small excess of sulphuric acid, carefully neutralizing the free acid with caustic potash, and washing the sulphate with cold distilled water until, on evaporating about 100 c.c. of the solution to dryness, and examining the residue according to the method about to be described, it yields no evidence of nitrates. The silver is, of course, recovered from these washings. If excess of sulphate of silver has been added, the residue usually becomes dark brown in colour. It should be tested by adding a drop of the sulphate; and if there is still a precipitate, a further quantity must be added until all the chlorine is thrown down. As soon as this is accomplished, and the contents of the dish evaporated to a very small bulk—some 5 or 10 c.c.—filter through a very small filter of Swedish or German paper, and wash several times with the smallest possible quantity of hot distilled water. The better to extract the nitrates from the dish, it is well to rub the residue off the surface with the end of the finger, protected by a caoutchouc finger-stall. The dish is readily cleaned by plunging it into dilute sulphuric acid and placing in contact with it a piece of zinc. By this means the silver is reduced to the metallic state, and most of it may be easily detached; the dish is then washed, and the remainder of the metallic silver removed by a bath of warm dilute nitric acid.

The filtrate is evaporated in a very small beaker to dryness, or nearly so, over a steam bath. The little apparatus shown in Fig. 9 is then placed in an ordinary porcelain mercury trough, and filled with mercury just above the stop-cock. The total length

Fig. 9.



of the tube is 210 m.m. and the internal diameter about 15 m.m. The concentrated solution, obtained as above, is then poured into the cup at the top of the tube; and the stop-cock being gently opened, it is allowed to flow down into the lower tube without

permitting air to follow. If evaporation has been carried to dryness the residue is treated with 1 or 2 c.c. of boiling distilled water, and the solution thus obtained run into the tube. The beaker is rinsed once with hot distilled water and twice or thrice with strong sulphuric acid, using as little as possible of water, and so much acid as to make up a volume which is to the total volume of water used as 3 : 2. If any air has been admitted, or, as sometimes occurs, any carbonic anhydride has been evolved, it can be sucked out of the tube into the cup. As soon as the beaker is rinsed out, hold the tube in the hand with the knuckles upward and the wet thumb closing the tube, and shake vigorously with a motion upwards and forwards in the direction of its length, so as to throw the mercury up into the acid solution, which latter should not be allowed to pass down to the thumb. Some of the mercury is soon finely divided, and if nitrates or nitrites are present nitric oxide is evolved; and when the pressure from within is considerable the thumb should be slightly, but not wholly, relaxed, some of the mercury being allowed to escape, but a certain amount of pressure still maintained within the tube. When no nitrates and nitrites are present the globules of mercury remain mobile and bright; but with a considerable quantity they break up on shaking into irregular masses, which adhere together, and look as if alloyed with some heavy metal. In the latter case it often happens that no gas is evolved for some little time; but it is at last produced with great rapidity, and at the close of the operation the finely divided mercury will, as in other cases, consist of minute spheres.

When the volume of gas ceases to increase it is decanted into the laboratory vessel of the gas apparatus, a stream of mercury allowed to pass over from the measuring tube to remove acid from the entrance to the capillary connecting tube, and the gas then passed over and measured. The weight of nitrogen present is calculated as in the determination of organic nitrogen; but as the gas measured is nitric oxide, which contains half its volume of nitrogen, it will be necessary to divide the result by 2.

If the quantity of ammonia present is greater than 0·1 part per 100,000, it is desirable to guard against loss of nitrogen by decomposition of ammonic nitrite during evaporation. Instead of employing the residue from the determination of the total solid matters, a fresh portion of the sample is taken, and to this, slightly acidified with dilute sulphuric acid, solution of potassic permanganate is gradually added until a pink colour is obtained, which will endure for about a minute. The liquid is then rendered slightly alkaline to test paper with sodic carbonate. Use as little as possible of each reagent. The nitrites being thus converted into nitrates the evaporation, with addition of sulphate of silver, may be proceeded with without fear of loss.

With waters containing an exceptionally large quantity of soluble matter (*e.g.* sea water), the preceding method is often inapplicable, as the volume of the liquid cannot be sufficiently reduced. If the quantity of the organic nitrogen be small—say, less than 0·1 part per 100,000—the following method may generally be used:—Take 200 c.c. of the sample, add to it 10 c.c. of a solution of caustic soda in a litre of water, and boil rapidly in an open porcelain dish until the volume is reduced to about 70 c.c. Allow to cool, and pour it into a tall glass cylinder of about 120 c.c. capacity, rinsing it with water free from ammonia. Sink in this solution, by means of a bent piece of heavy glass rod, a piece of thin clean aluminium foil, close the cylinder with a cork perforated with one opening, in which is fixed a small glass tube filled with fragments of clean recently ignited pumice, moistened with a few drops of dilute hydrochloric acid free from ammonia. This tube should be covered by a test tube or very small beaker. In from four to six hours the whole of the nitrates and nitrites are reduced, the nitrogen being converted into ammonia. The contents of the cylinder and of the pumice tube are washed into a small retort, the cylinder and tube being well rinsed with water free from ammonia; and the ammonia produced is distilled over and estimated in the usual way with Nessler's solution. A correction based on several blank experiments should be applied to correct for the small quantity of ammonia which appears to be inevitably present in the reagents and apparatus. The caustic soda solution should be prepared as follows:—Dissolve 100 grams. of solid caustic soda in a litre of distilled water; when cold, put the solution in a tall glass cylinder, and add about 100 sq. c.m. of aluminium foil, keeping it at the bottom with a glass rod. As soon as this is dissolved, boil until about one-third of its volume has been drawn off, allow to cool, and make up to the original volume with water free from ammonia.

Hydrochloric acid is sufficiently pure if two or three drops do not contain an appreciable quantity of ammonia. If this is not already the condition of the ordinary pure acid, it should be rectified over sulphuric acid.

The nitrogen as nitrates may be more rapidly estimated by means of a standard solution of indigo in presence of strong sulphuric acid at a high temperature. This process, originally proposed by Marx and improved by Sutton, has recently been very elaborately investigated by Warington; and although it does not rival the mercury method in accuracy, it will in many cases be sufficient for the purpose in view, while its rapidity and simplicity greatly recommend it. No gas apparatus is required, and it is not necessary to concentrate the sample to be examined.

The indigo solution is made by dissolving pure soluble indigo-carmine (or according to Warington, indigotine) in distilled water. A convenient strength is one of which 10 c.c. is decolorized by 10 c.c. of a standard solution of pure potassic nitrate containing 0·02 gram. of nitrogen, or 0·14442 gram. of KNO_3, per litre. The exact value of the indigo solution in terms of nitrogen as nitrates, must be ascertained by experiments precisely similar to those by which the samples of water are examined.

Ten c.c. of the water to be examined are measured into a thin flask of about 150 c.c. capacity, then about 30 c.c. of strong sulphuric acid (spec. grav. at least 1·8) rapidly added, the mixture shaken, and standard indigo solution run in from a burette until a greenish tint is obtained. This must be done as rapidly as possible, and without any attempt at minute accuracy, the object being merely to ascertain the approximate quantity of indigo required. If this be much more than 10 c.c. it is best in subsequent experiments to employ a proportionately smaller quantity of the water, and dilute it to 10 c.c. with distilled water. In such experiments add to the measured quantity of water (thus diluted, if necessary) the quantity of indigo solution judged from the first experiment to be required, bearing in mind that the first result is probably too low. Having mixed these, measure out a quantity of sulphuric acid equal to twice their united volume, add rapidly, and shake. If after about a minute the colour is dark red, somewhat like sherry, more indigo should be added. With excess of indigo the colour becomes brown, and then greenish. The first tint of brown should be taken as indicating the proper quantity of indigo. Successive trials should be made until this tint is obtained on first mixing, without supplementing the quantity of indigo taken. The quantity of sulphuric acid mentioned above, viz., two volumes, is that recommended by Sutton and used by the writer; but Warington suggests that half that proportion should be used, and says that the tint is more easily observed, being, while the nitrates are in excess, deep reddish, changing when the indigo is in excess to dull brown, and then greenish, the first appearance of brown being taken as the critical point. The sulphuric acid must be free from sulphurous acid, and from nitrous bodies. The former, if present, may be expelled by heating in an open flask for some hours nearly to the boiling point; and the latter by the addition of a little oxalate of ammonia, and subsequent heating as before.

When organic matter of animal origin is exposed to the action of oxygen, its nitrogen is rapidly converted for the most part into nitric and nitrous acids, which, uniting with bases in the soil, form nitrates and nitrites. When the aëration is ample, as in passing through a porous soil, nitrates are almost exclusively formed. Organic matter of vegetable origin yields no nitrates or nitrites, or mere traces of them. Hence, the proportion of nitrogen as nitrates and nitrites, themselves innocuous, is a trustworthy indication of the extent of the pollution by animal matters to which the water has been subjected. In upland surface water the proportion varies from *nil* to about 0·05, with an average of about 0·01 part per 100,000. In surface waters from cultivated districts the pollution from manure applied in agricultural operations, from the drainage of farm-yards, &c., raises the proportion considerably—varying from *nil*, which is rare, to about 1 part, with an average of about 0·25 part per 100,000. In the neighbourhood of shallow wells the pollution, for reasons which have been previously pointed out, is generally more concentrated, and the quantity of nitrates and nitrites is consequently much greater; all proportions having been observed up to 25 parts, from 2 to 5 parts being, perhaps, most frequent. Deep well and spring water contains from *nil* up to about 3 parts, with an average of 0·5 part per 100,000, that in spring water being somewhat lower than in deep well water. In some cases, especially in deep well waters, nitrates are subsequently reduced by organic matter, or even wholly obliterated. They are likewise rapidly destroyed during the putrefaction of sewage, and hence it is rarely the case that any nitrates are found in sewage, unless it is extremely weak, or otherwise abnormal.

Total Combined Nitrogen.—This number is obtained by adding together the amounts of the organic nitrogen, and nitrogen as ammonia and as nitrates and nitrites. The first of these represents the actual or *present* contamination of the water as regards animal matter, the others the past pollution, and their sum the total pollution. It must be remembered, however, that all these are *minima;* we can only say that the amount of pollution was *at least* so much, while the evidence of further contamination may have disappeared, a loss of nitrogen taking place both in the oxidation of organic matter and, as observed in the preceding paragraph, in the reduction of nitrates and nitrites.

Previous Sewage, or Animal Contamination.—It has been found convenient to express the amount of contamination to which a water has been subjected, as indicated by the ammonia and nitrates and nitrites which it contains, in some concrete form. For this purpose London sewage has been selected, and the water is said to exhibit, in 100,000 parts, a quantity of previous sewage or animal contamination equal to so many parts of London sewage. That is to say, 100,000 parts of the water contain the mineral residue of an amount of animal organic matter equal to that found in so many parts of average London sewage. For this purpose, which it will be seen is to a great extent conventional, it is assumed that such sewage contains 10 parts of total combined nitrogen in 100,000. This is larger than the actual quantity, a round number being taken for convenience; the amount in 1857, according to Hofmann and Witt, being 8·363 parts, and in 1868 and 1869, according to the Rivers Commission, 7·06 parts. Since rain water contains a certain quantity of ammonia and of nitrates and nitrites, a correction is applied for this. When the estimation was first proposed, this correction was made by the deduction of 0·032 part, and subsequent analyses of water collected with especial care at Rothamsted during the years 1869 and 1870 confirm this, the number obtained being ·034 part. The previous sewage or animal contamination of a water is then calculated, by multiplying the sum of the nitrogen as ammonia, and as nitrates and nitrites, by 10,000 and deducting 320. This previous contamination does not indicate actual, but possible danger, arising from the risk lest some portion of noxious matter may escape

destruction and produce disease in the person who drinks the water. This risk increases with the increase of the proportion of original contamination. It is greater in the water of rivers and shallow wells than in that of deep wells and springs. In river water the polluting matter may be carried down the stream, and undergoing in such circumstances only slow decomposition may altogether escape, and in the case of shallow well water the oxidation, although rapid and generally energetic, is but brief in duration and subject to great variations from changes of meteorological and local conditions; so that at short notice, the oxidising action being suspended, that which was recorded as *previous* contamination may become *actual* and *present*. In the cases of deep wells and springs the risk is much less, since, as has been previously pointed out, the conditions are practically permanent and the oxidation very long continued. Waters may be classified as regards this consideration as follows:—

Reasonably Safe Water: derived from deep wells or deep-seated springs, surface water being rigidly excluded, and the proportion of previous sewage contamination not exceeding 10,000 parts.

Suspicious or Doubtful Water: shallow well, river, or flowing water with any proportion, however small, of previous sewage contamination; and deep well or spring water containing from 10,000 to 20,000 parts.

Dangerous Water: shallow well, river, or flowing water with more than 20,000 parts of previous sewage contamination, or containing less than that, but known to receive sewage either discharged directly into it or mingling with it as surface drainage; and deep well, or deep-seated spring water with more than 20,000 parts of previous sewage contamination.

In upland surface waters there is usually no evidence of previous sewage contamination; in surface water from cultivated land it may amount to 10,000, the average being about 2000; in shallow wells it is usually large, and has been observed as great as 250,000, or derived from a water with a pollution 2½ times as great as that of London sewage. Frequently occurring quantities are 10,000 to 50,000 parts. In deep well and spring waters it ranges up to 35,000, with an average for deep wells of 5000, and for springs of 4000.

Suspended Matters.—A convenient volume of the sample is filtered through a weighed filter, which is then dried at 120° to 130° C., weighed again to ascertain the total weight of suspended matter, and finally incinerated to determine the weight of mineral suspended matter. A quarter of a litre or less is usually enough of sewage, and when the quantity is so small that a litre does not contain sufficient to weigh, the determination is seldom necessary. The filter used should be of Swedish or German paper, which has been previously treated with dilute hydrochloric acid, and then washed with hot distilled water until all chlorides have been removed; the ash is by this means reduced to about one-third of its original weight, and it should be carefully determined for each sample of paper by incinerating ten of the washed filters and weighing the ash. Filtration is much accelerated by ribbing the filters. They should be dried in an air bath at 120° to 130° C. (best maintained by means of a mercurial thermostat) for about three hours, and then separately weighed and returned to the bath for another hour and again weighed, repeating this until the loss of weight during an hour's drying does not exceed 0·0003 gram. To protect them during the time of cooling and weighing, each one is inclosed in a pair of thin glass tubes fitting closely one into the other, each about 50 m.m. long and closed at one end. These are easily made from test tubes; the edge at the open end should be smoothed by heating before the blow-pipe, and each pair should bear a distinctive number marked on both tubes with a writing diamond. While in the water oven they should be supported in a grooved tray made by folding up a piece of clean perforated zinc, the tubes being drawn apart, and the filter drawn nearly but not quite out of the inner tube, the point of the filter being outwards. They should be allowed twenty minutes to cool under a desiccator before weighing. Much time may be saved by placing the liquid to be filtered in a narrow-necked flask, and inverting this in the filter so as to make it self-supplying. The flask is supported by a ring stand, a slot being cut through the ring to allow the neck of the flask to pass after inversion. When the whole of the liquid has passed through, the flask should be rinsed out with a little distilled water, and the rinsings added to the filter. The latter is dried for a short time at 100° C., and then transferred to the same pair of tubes in which it was previously weighed, and a second time dried at 120° to 130° C. until the weight is constant; this weight, minus that of the dried empty filter and weighing tubes, gives us the total weight of the suspended matter dried at 120° to 130° C. Finally, the filter is incinerated in a platinum crucible, when the weight of the ash, less that of the filter ash, gives the weight of mineral suspended matter in the quantity of water taken.

Chlorine as Chlorides.—Add to 50 c.c. of the sample contained in a small flask, two or three drops of a strong solution of pure potassic chromate, and then add gradually, from a narrow burette, a standard solution containing 2·3944 grams. of pure recrystallized argentic nitrate per litre, until the red colour produced, as each drop is added, ceases to disappear on shaking, and the whole solution has a very faint red tint. As 1 c.c. of the above standard solution corresponds to 0·0005 gram. of chlorine, the number of c.c. of the standard solution used will, when 50 c.c. of water are used for the experiment, indicate the number of parts of chlorine present in 100,000 parts of the water. Accuracy may be increased if necessary by adding, at the conclusion of the experiment, a trace of a soluble chloride to destroy the red colour, and using this flask as a standard of comparison in making a second experiment. As both flasks will exhibit about the same quantity of precipitate and the same yellowish hue, the smallest tinge of red can be readily detected. It is necessary

that the liquid to be examined should not be acid unless with carbonic acid, nor more than slightly alkaline, and it must be colourless or nearly so. If this is not the case add lime water free from chlorine until slightly alkaline, saturate with carbonic anhydride, boil and filter. This is in most cases successful; but if not, evaporate the alkaline liquid to dryness, ignite gently to destroy organic matter, extract with water, filter and estimate the chlorine in the solution.

Chlorides are occasionally derived from the rocks over and through which the water passes, but more generally from animal excreta. Human urine contains about 500 parts of chlorine per 100,000. Unpolluted waters generally contain less than 1 part; shallow well water, all proportions up to 50 parts, or even more; average town sewage about 11 parts. Filtration or other methods of purification have seldom any action on the quantity of chlorides present. Subject to the consideration of the nature of the rocks from which the water comes, and proximity to the sea or other source of chlorine, a water containing more than 3 or 4 parts of chlorine should be regarded as suspicious.

Hardness.—The process introduced by Dr. CLARK of Aberdeen is universally employed for the estimation of hardness. It consists in observing the quantity of a solution of soap of known strength which is required to produce a permanent lather after violent shaking in a bottle with a measured volume of water. The soap solution originally used was made by dissolving white curd soap in proof spirit; but as this soap is not very soluble it does not form a very satisfactory solution, and one of neutral potash soap is much more convenient. It is made by scraping lead plaster (*Emplast. Plumbi* of the druggist) so as to obtain it in a moderately finely divided state, and mixing it in a mortar with dry potassic carbonate in the proportion of 150 parts of the former to 40 parts of the latter. When mixed add some methylated spirit, and rub well in the mortar until a smooth mixture is obtained of about the consistency of thick cream. After standing for several hours, filter and wash the insoluble matter with methylated spirit. A very strong alcoholic solution of neutral potassic soap is thus obtained, which must be diluted with a mixture of 1 volume of distilled water and 2 volumes of methylated spirit, reckoning the strong soap solution as spirit, until exactly 14·25 c.c. correspond to 50 c.c. of the standard solution of calcic chloride presently to be described. It is best to make it somewhat too strong at first, and after ascertaining its strength dilute it to the required extent. When nearly of the right strength, but still rather too strong, it should be allowed to stand for twenty-four hours; then, if not perfectly clear, filtered; and then accurately adjusted to the required strength. In estimating the strength of the solution, the process and apparatus employed in estimating the hardness of waters should be rigidly adhered to.

The standard calcic chloride solution is made by dissolving 0·2 gram. of pure crystallized calcite in dilute hydric chloride in a platinum dish, and evaporating to dryness, taking care to avoid loss by spirting. To remove all free hydric chloride, water is several times added, and the evaporation to dryness repeated. The residue is then dissolved in distilled water, and made up to 1 litre.

The estimation of hardness is made thus:—50 c.c. of the water are shaken violently for some few seconds in a well-stoppered glass bottle of about 250 c.c. capacity, and then the air is renewed in the bottle by means of suction through a glass tube, in order to remove any carbonic anhydride which may have been set free. Add then from a burette the standard soap solution, using 1 c.c. at a time, and shaking after each addition, until, when the bottle is after shaking placed at rest on its side, a thin but continuous lather extends over the whole surface for five minutes. Towards the end of the operation less than 1 c.c. should be added at a time, but never more than that quantity. If more than 16 c.c. are required, another experiment should be made with a less quantity of the water, the same volume of 50 c.c. being made up by recently boiled distilled water. If much magnesium is present the lather exhibits a peculiar curdy appearance, and in such cases water should be added if necessary, so that not more than 7 c.c. of soap solution are used.

The quantity of soap solution required to give a permanent lather with 50 c.c. of the water being thus ascertained, the hardness expressed in parts of calcic carbonate ($CaCO_3$) per 100,000 may be taken from the following table V. on page 981, which has been calculated from CLARK's original table given in the foot-note.*

Hardness of water is said to be of two kinds, *temporary* and *permanent*. The former is that due to the presence of calcic and magnesic carbonates held in solution by carbonic acid, and is termed *temporary*, because by long-continued boiling the carbonic acid is expelled and the carbonates precipitated.

* CLARK'S TABLE OF HARDNESS.

Degree of Hardness.	Measures of Soap Solution.	Difference for the next Degree of Hardness.	Degree of Hardness.	Measures of Soap Solution.	Difference for the next Degree of Hardness.
0	1·4	1·8	9	19·4	1·9
1	3·2	2·2	10	21·3	1·8
2	5·4	2·2	11	23·1	1·8
3	7·6	2·0	12	24·9	1·8
4	9·6	2·0	13	26·7	1·8
5	11·6	2·0	14	28·5	1·8
6	13·6	2·0	15	30·3	1·7
7	15·6	1·9	16	32·0	—
8	17·5	1·9	—	—	—

This table may be used if it is desired to express results in grains per gallon. Each "degree" of hardness corresponds to 1 grain of calcic carbonate ($CaCO_3$) per imperial gallon (70.000 grains) of water. Each "measure" equals 10 grains of distilled water. The soap solution described in the text is of exactly the same strength as that employed by Dr. CLARK, and may therefore be used with either table. When the number of the grain "measures" of soap solution does not correspond exactly with any of the above degrees, the fraction of a degree must be calculated from the difference given in the third column.

TABLE OF ILLUSTRATIVE ANALYSES—RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

Description.	Total solid Matters.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Previous Sewage or Animal Contamination. (Estimated).	Chlorine.	Hardness. Temporary.	Hardness. Permanent.	Hardness. Total.	Remarks.
UPLAND SURFACE WATERS.												
Chester, Water supply of, May 19, 1873,	16·84	·219	·043	—	—	·043	—	2·00	5·0	5·7	10·7	Turbid.
Machynlleth, Stream near, Oct. 1877,	2·60	·110	·009	—	—	·009	—	·73	—	—	·95	Clear.
Bournemouth, Water supply of, March 11, 1873,	5·92	·282	·039	—	—	·039	—	2·35	—	1·8	1·8	Clear.
Saltaire, Water supply of, Jan. 26, 1874,	12·36	·189	·027	—	—	·027	—	1·30	—	7·3	7·3	Slightly turbid.
Glasgow, Loch Katrine service, Jan. 15, 1878,	3·10	·215	·021	—	·005	·026	—	·53	—	—	1·2	Light brown, slightly turbid.
SURFACE WATER FROM CULTIVATED DISTRICTS.												
Taunton, Water sup. of, Sept. 4, 1873,	8·58	·254	·035	·001	·183	·219	1,520	1·50	—	2·6	2·6	Slightly turbid.
Barnstaple, " Oct. 1, 1872,	9·94	·126	·018	—	·098	·116	660	1·55	—	5·9	5·9	Clear.
Wigan, " May 10, 1874,	22·38	·294	·070	·003	·079	·151	490	1·90	1·7	13·5	15·2	Slightly turbid.
Granton, " Mar. 24, 1873,	39·88	·216	·053	·002	·269	·324	2,390	3·40	14·9	12·6	27·5	Clear.
Basingstoke, River Loddon at, Feb., 1877,	31·50	·180	·027	·002	·454	·483	4,240	1·36	18·6	4·1	22·7	Turbid.
SHALLOW WELLS.												
Liskeard, Dean well, Sept. 23, 1873,	15·84	·063	·024	—	·591	·615	5,590	3·50	—	7·7	7·7	Clear.
Birmingham, Court in Stamforth Street, Sept. 18, 1873,	194·80	·454	·186	·014	6·437	6·635	64,170	37·50	26·3	66·6	92·9	Slightly turbid.
Birmingham, Court in Watery Lane, March 20, 1876,	351·60	—	very large.	1·500	23·100	—	243,030	41·13	—	—	—	Clear.
Deal, Pump in Market Place, Aug. 28, 1873,	146·00	·241	·034	1·700	6·345	7·779	77,130	19·20	33·0	34·3	67·3	Clear. Slight saline taste.
London, Pump at St. Martin's Ch., Charing Cross, June 4, 1872,	96·50	·159	049	—	4·911	4·960	48,790	10·50	21·6	21·2	42·8	Clear.
Guildford, Water supply of, Oct. 4, 1873,	28·58	·060	·017	—	·413	·430	3,810	1·80	14·5	7·0	21·5	Clear.
Peterborough, Town pump, June 11, 1873,	213·80	·321	·113	—	7·768	7·881	77,360	22·10	27·3	64·3	91·6	Clear. Slight saline taste.
Tottenham, Shallow well at, Sept. 21, 1877,	91·44	·310	·077	—	3·074	3·151	30,420	5·30	7·0	30·7	37·7	—
DEEP WELLS.												
Woodlesford, near Leeds, Aug. 1877,	77·80	·142	·024	·009	—	·031	—	15·00	·9	—	·9	Turbid, 360 feet.
Ashby de la Zouch, Prior Park, 1877,	44·20	·059	·012	—	·448	·460	4,160	6·15	5·8	22·7	28·5	Slightly turb., 42 ft.
Maidenhead, Brewery, May, 1876,	41·36	·056	·015	·012	·866	·891	8,440	2·20	20·3	9·7	30·0	Clear.
Broadstairs, New supply, Oct. 1876,	47·32	·073	·012	—	·627	·639	5,950	7·05	22·1	6·5	28·6	Turbid.
Maldon (Essex), Water supply of, Jan. 3, 1877,	119·00	·148	·029	·110	—	·120	590	35·80	2·5	1·4	3·9	Slightly turbid, 237 feet.
SPRINGS.												
Chewton Mendip, head spring of River Chew, Feb. 19, 1877,	28·00	·063	·014	·002	·169	·185	1,390	89	17·6	4·2	21·8	A few suspended particles.
Woodlesford, near Leeds, 1877,	98·72	·294	·111	·002	·846	·959	8,160	0·50	10·8	41·4	52·2	Slightly turbid—lead in solution.
LONDON WATER SUPPLY—Average of monthly analyses during nine years, 1868–76.												
From the Thames,	27·80	·203	·033	·0007	·208	·241	1,766	1·75	—	—	20·5	—
From the Lea,	27·80	·129	·023	·0005	·198	·222	1,683	1·78	—	—	21·0	—
From deep wells in the chalk,	40·88	·047	·012	·0002	·419	·431	3,875	2·42	—	—	28·1	—
BIRMINGHAM WATER SUPPLY.												
Average of monthly analyses during 1876,	25·13	·266	·063	·002	·230	·295	1,990	1·71	6·3	10·2	16·5	—
GLASGOW WATER SUPPLY—From Loch Katrine.												
Average of monthly analyses from March, 1877, to Feb. 1878,	2·96	·186	·011	—	·004	·016	—	0·67	—	—	0·95	—
Norwegian Block Ice, fr. Wear Ice Wharf, Sunderland, April, 1877,	·37	·029	·005	·005	—	·009	—	·05	—	—	—	Clear.
AVERAGE COMPOSITION OF UNPOLLUTED WATER.												
Rain water, 39 samples,	2·95	·070	·015	·029	·003	·042	42	·22	—	—	·3	—
Upland surface water, 195 samples,	9·67	·322	·032	·002	·009	·043	—	1·13	1·5	4·3	5·4	—
Deep well water, 157 samples,	43·78	·061	·018	·012	·495	·523	4,730	5·11	15·8	9·2	25·0	—
Spring water, 198 samples,	28·20	·056	·013	·001	·383	·397	3,520	2·49	11·0	7·5	18·5	—
Sea water, 23 samples,	3898·7	·278	·165	·006	·033	·203	60	1975·6	48·9	748·0	796·9	—

TABLE V.—TABLE OF HARDNESS, 50 C.C. OF WATER USED.

Soap solution, c.c.	$CaCO_3$, per 100,000.	Soap solution, c.c.	$CaCO_3$, per 100,000.	Soap solution, c.c.	$CaCO_3$, per 100,000.	Soap solution, c.c.	$CaCO_3$, per 100,000.	Soap solution, c.c.	$CaCO_3$, per 100,000.
0·7	·00	3·8	4·29	6·9	8·71	10·0	13·31	13·1	18·17
·8	·16	·9	·43	7·0	·86	·1	·46	·2	·33
·9	·32	4·0	·57	·1	9·00	·2	·61	·3	·49
1·0	·48	·1	·71	·2	·14	·3	·76	·4	·65
·1	·63	·2	·86	·3	·29	·4	·91	·5	·81
·2	·79	·3	5·00	·4	·43	·5	14·06	·6	·97
·3	·95	·4	·14	·5	·57	·6	·21	·7	19·13
·4	1·11	·5	·29	·6	·71	·7	·37	·8	·29
·5	·27	·6	·43	·7	·86	·8	·52	·9	·44
·6	·43	·7	·57	·8	10·00	·9	·68	14·0	·60
·7	·56	·8	·71	·9	·15	11·0	·84	·1	·76
·8	·69	·9	·86	8·0	·30	·1	15·00	·2	·92
·9	·82	5·0	6·00	·1	·45	·2	·16	·3	20·08
2·0	·95	·1	·14	·2	·60	·3	·32	·4	·24
·1	2·08	·2	·29	·3	·75	·4	·48	·5	·40
·2	·21	·3	·43	·4	·90	·5	·63	·6	·56
·3	·34	·4	·57	·5	11·05	·6	·79	·7	·71
·4	·47	·5	·71	·6	·20	·7	·95	·8	·87
·5	·60	·6	·86	·7	·35	·8	16·11	·9	21·03
·6	·73	·7	7·00	·8	·50	·9	·27	15·0	·19
·7	·86	·8	·14	·9	·65	12·0	·43	·1	·35
·8	·99	·9	·29	9·0	·80	·1	·59	·2	·51
·9	3·12	6·0	·43	·1	·95	·2	·75	·3	·68
3·0	·25	·1	·57	·2	12·11	·3	·90	·4	·85
·1	·38	·2	·71	·3	·26	·4	17·06	·5	22·02
·2	·51	·3	·86	·4	·41	·5	·22	·6	·18
·3	·64	·4	8·00	·5	·56	·6	·38	·7	·35
·4	·77	·5	·14	·6	·71	·7	·54	·8	·52
·5	·90	·6	·29	·7	·86	·8	·70	·9	·69
·6	4·03	·7	·43	·8	13·01	·9	·86	16·0	·86
·7	·16	·8	·57	·9	·16	13 0	18·02	—	—

Permanent hardness is that due to the presence of sulphates, chlorides, &c., which cannot be so precipitated. To estimate permanent hardness, boil about 160 c.c. in a small flask for half an hour, and then make up to the original volume with recently boiled distilled water, filter when cold through a dry filter, and determine the hardness as before described. This permanent hardness, deducted from the "total hardness," gives the amount of "temporary hardness." During the boiling the steam should be allowed to escape freely, otherwise carbonic anhydride will be retained and the whole of the carbonate of lime not precipitated. It is less trouble to make up the flask and water always to the same weight, say, 200 grams., both before and after boiling, than to measure the quantity used.

The hardness of water varies according to the extent of its pollution with animal matter (since animal refuse contains a large proportion of lime), and according to the strata over or through which it passes. Igneous rocks yield the softest water, the average hardness of water from them being about 2·4 parts; and chalk and dolomite the hardest, with an average in the latter of about 41 parts. Shallow well waters are generally extremely hard, nearly 200 parts having been observed.

The Alleged Self-Purification of Polluted Rivers.—Since so many of our streams are used both as sources of water supply and as means for removal of sewage, the consideration whether polluting matter introduced into them is or is not destroyed by oxidation or other purifying actions occurring in running water is of the highest importance.

Running water has from time immemorial been popularly considered to be necessarily pure; and more recently it has been frequently asserted, with more or less emphasis, but without any attempt at proof, that if ordinary London sewage be mixed with "twenty times its bulk of the ordinary river water, and flows a dozen miles or so, there is not a particle of that sewage to be discovered by any chemical processes."

Several opportunities for the examination of this question occurred during the investigations of the late Royal Commission on the pollution of rivers; and the results obtained all demonstrated, by quantitative proofs which have never been called in question, the fallacy of the assertion just stated. Of these investigations we will briefly mention two, illustrated by the following analyses:—

RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

Description.	Total Solid Matters.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Chlorine.	Suspended Matters.			Temperature of Water, C.
								Mineral.	Organic.	Total.	
River Irwell at Throstlenest Weir, May 13, 1869,	39·1	2·156	·238	·140	—	·353	4·9	1·18	1·86	3·04	12·2
" at junction with Mersey, "	43·0	2·374	·210	·250	—	·416	6·4	1·88	2·40	4·28	13·3
" at Throstlenest Weir, June 11, 1869,..	63·5	2·134	·239	·375	—	·548	13·0	2·66	2·72	5·38	17·8
" at junction with Mersey, "	61·5	1·502	·241	·413	—	·581	12·9	2·28	1·88	4·16	17·8
River Thames, half mile below junction with the Kennet, May 31, 1873,.....	28·86	·261	·071	·007	·167	·244	1·70	·42	·06	·48	16·7
River Thames, just above Shiplake Paper Mill, May 31, 1873,.....	28·42	·245	·068	·007	·155	·229	1·70	·14	·10	·24	16·7

The Irwell after passing Manchester falls over a weir at Throstlenest, and then runs eleven miles to its junction with the Mersey without further material pollution, and with the addition of but very unimportant unpolluted affluents, passing on its way, moreover, six weirs with a total height of 34½ feet, by which means it is abundantly aërated. Considering that, owing to the differences in the velocity of different parts of the current in the same transverse section, it is impossible to follow precisely the same volume of water during its passage down the stream, these numbers are sufficiently conclusive in the case of this highly polluted stream. At a nearly average temperature and with abundant aëration, the change in the organic matter produced by a run of eleven miles was, in the first case, a reduction of

the organic nitrogen by 11·8 per cent., the organic carbon being slightly higher; and in the second case, a reduction in the organic carbon of 29·6 per cent., the organic nitrogen being practically unaffected.

The Thames was selected as an instance of a river which was polluted in a much smaller degree than the Irwell, and the experiments were made when aquatic vegetation was very active in its bed. After receiving the waters of the Kennet, the Thames flows for about four miles to Shiplake Mill without receiving any other affluent or pollution of importance. The samples were taken on a bright sunny day in May, and as the water of the Kennet flows for some distance at one side of the main stream without thoroughly mingling with it, the upper sample was taken by instalments in crossing the river in a boat about a quarter of a mile below the junction of the Kennet. About two miles below this point the river passes the weir and rapids at Sonning, and is there thoroughly aërated and mixed. The interval between the taking of the two samples was approximately equal to the time occupied by the stream in passing between the two places. It will be seen that very little change has taken place; the organic carbon has been reduced by about 6 per cent., and the organic nitrogen by about 4. If the reduction continued at this rate night and day, in sunshine and gloom, it would require a flow of about seventy miles to remove the organic matter in the Thames after its junction with the Kennet.

Subsequent experiments in the laboratory confirmed these results, and led to the conclusion that there is no river in England long enough to purify sewage in this way.

It will be seen that although the dissolved impurities are thus persistent, the amount of suspended matter is very considerably diminished during the flow of a river. This, however, is not removed, but deposited in the bed of the river, and during floods may be again stirred up, or during hot weather, as in the case of the Irwell, enter into active putrefaction.

Dissemination of Disease by Potable Water.—It can no longer be doubted that many diseases are spread by means of living germs which, introduced into the animal organization, multiply and produce the specific disorder characteristic of a disease of the so-called *zymotic* class (from ζύμωσι, "I ferment"). Although the truth of this opinion has not yet been experimentally demonstrated in all cases, yet the experiments of M. Chauveau in 1868, confirmed by those of Dr. Burdon-Sanderson, proved that the specific poison of many of these diseases is not in solution, but in suspension in the liquid virus. It was found that when the virus of vaccine matter—small-pox, sheep-pox, or glanders—was filtered, or allowed to stand for a long time to deposit suspended matter, the filtrate or decanted liquor was still powerfully infectious. When submitted to diffusion in distilled water, the soluble matters were removed in the water and were found to be powerless for inoculation, while the liquid containing the suspended matter, but free from the soluble matters of the virus, was as powerfully infectious as before. In vaccinating with very dilute lymph it is evident that sometimes the liquid introduced into the system might not contain a single germ and would therefore be abortive; but if only one germ was successfully introduced, its indefinite multiplication would make it as effective in producing the disease as a larger number of germs. If, on the other hand, the poison were in the solution, then dilution should reduce the virulence of the disease caused by inoculation. Experiment abundantly proved that dilution of the virus diminished the proportion of successful inoculations, but did not affect the intensity of the disease in those cases which were successful. More recently the experiments of Cohn and Koch have shown that splenic fever in animals, and malignant carbuncle in man, are produced by a peculiar species of bacterium, the *Bacillus anthracis;* and Dr. Burdon-Sanderson has shown that in twenty-four hours a single bacillus multiplies by bisection into 17,000,000 of separate bacilli.

It is true that a large proportion of those who are exposed to the infection of zymotic poisons yet escape disease. The circumstances are not favourable to the development of the germs, or the constitution of the subject is such as enables him to resist its influence. Nevertheless an overwhelming weight of well-attested evidence points to the conclusion that disease is conveyed from one individual to another, that water carriage is very favourable to this transference, and that the water supply of towns and villages is of such a nature, and so connected with the disposal of sewage matters, as to greatly facilitate it. It is well ascertained that the infectious poison of such diseases as cholera and typhoid fever resides in the intestinal discharges; and it is a common, almost universal, practice to throw sewage containing human excreta into streams or cesspools, and to take drinking water from the same streams or from wells in the immediate vicinity of the cesspools. Thus a large proportion of the population is daily exposed to risk of infection from typhoidal, and periodically to that from choleraic discharges. Evidence that cholera and typhoid fever are disseminated by water carriage might be adduced to an enormous extent; but we will here briefly mention only a few instances which, from the circumstances under which they occurred, and the completeness with which they were investigated, afford most cogent proof.

Dissemination of Cholera by Water.—The Epidemic in St. James', Westminster, in 1854.—On the morning of Friday, September 1st, 1854, cholera broke out in this district with terrible violence, the centre of the pestilence appearing to be between Broad Street and Silver Street. Out of an estimated population in Broad Street of 860 persons, ninety died, besides twenty-five others who worked there, but died in other parts of London. A certain well-defined area, which was afterwards called the "cholera area," contained about 14,000 inhabitants in 825

houses, and in this area 618 fatal cases occurred in 313 houses. The cause of this frightful mortality was ascertained to be the water from a pump in Broad Street, at about the centre of the above area. It was found that a house drain ran within 2 feet 8 inches of this well, at a height of about 9 feet above the water line; and about seventy-eight hours before the outburst a child was fatally attacked with choleraic diarrhœa, and its dejections were thrown into a choked and full cesspool communicating with this drain. A subsequent investigation showed that sixty-one out of seventy-three persons who died during the first two days had been accustomed to drink the water of this well either constantly or occasionally; that in a factory employing 200 people, where the water was drunk daily, eighteen people died, while, at a neighbouring brewery, the seventy men employed did not drink this water, and escaped cholera; that in many individual cases it was found that the drinking of the water was followed by cholera—in one case, a lady who had removed to Hampstead, was so accustomed to the water that she had it sent to her, and died in consequence, together with her niece; that at any point decidedly nearer to another pump, the mortality from cholera as a rule ceased, and that out of forty-eight apparent exceptions to this rule, in which cases deaths had taken place nearer to another pump, many were found to be those of persons who had a preference for the more distant Broad Street water; that in one street of fourteen houses the only four which escaped without a death were those in which the water was never drunk; that with but a single exception the water was used for drinking purposes only, and was used cold.

Epidemic at Theydon Bois, Essex, in 1865—This case was investigated by J. Netten Radcliffe on behalf of the Privy Council. The head of the family in which it occurred, and his wife, after a fortnight's absence from home, returned from Weymouth by way of Southampton, cholera having appeared in the latter town eight days before. The day after their return the wife was seized with diarrhœa, and the husband also suffered in a less degree. Both used a water closet, between the soil pipe of which and the well supplying the house with drinking water, there was afterwards found to be free communication. This water was used for drinking for fully five days, and out of twelve cases nine ended fatally. Only one person escaped without any indisposition.

Dissemination of Typhoid Fever by Drinking Water. —Millbank Prison, London.—Up to the 10th of August, 1854, this prison had been supplied with water pumped from the river Thames as it passed the prison, and purified by filtration. For many years the place had been extremely unhealthy; epidemics of typhoid fever, diarrhœa, and dysentery were of frequent occurrence. In the ten years from 1845 to 1854 there were fifty-seven deaths recorded as from typhoid, and the three epidemics of cholera in 1833, 1849, and 1853-55 were very fatal. On August 10, 1854, a new supply of water from the Artesian well in Trafalgar Square was introduced in place of that from the Thames, and at once a marked change took place. It was in the midst of the cholera epidemic, and six days afterwards that disease suddenly ceased in the prison. The prisoners entirely escaped the cholera epidemic of 1866, and in the eighteen years from 1854 to 1872 (the date of the report from which these facts are taken) only three deaths occurred from typhoid fever, one in each of the years 1855, 1860, and 1865, the last being that of a convict who had the disease at the time of his admission. In the twelve years from 1843 to 1854 the total annual death rate was 33 per 1000, while in the sixteen years from 1855 to 1870 it was only twelve per 1000.

Epidemic at Cowbridge, South Wales.—In November, 1853, two public balls were held at the chief hotel in Cowbridge, at which about 140 persons were present from the surrounding district, and also from Gloucester, Somerset, and other distant counties. A few days afterwards an outburst of typhoid fever occurred amongst the visitors, and altogether about forty or fifty suffered from it, eight of whom died. These cases, scattered over so large an area, had one fact in common—the patient had been at the Cowbridge balls. On subsequent investigation by Dr. W. Budd, F.R.S. (from whose work on "typhoid fever" these facts are taken), it was found that just previous to the balls a gentleman staying in the hotel had been laid up with typhoid fever, and had left a day or so before the balls, not yet fully convalescent. The diarrhœal discharges from the patient had been thrown into a cesspool and drain, which were so near the well supplying the hotel with water that, under the conditions of soil and locality, percolation from one to the other was almost inevitable. This defect has since been remedied; but at the time of the balls in question, the water of the well thus dangerously situated was used for the preparation of various beverages, such as lemonade, freely consumed by the visitors.

As was previously stated, illustrations such as these might be multiplied to a very large extent; but those which have been thus briefly recounted are so well established and ascertained, that it is not necessary to adduce further evidence to prove that the use of water for dietetic purposes, to which excreta have had access, is fraught with the gravest possible risk to health and even to life.

On the Influence of Hardness of Water upon Health. —Much discussion has occurred among medical men and others whether hard or soft water is better for health. Hard water has been charged with the production of goitre, calculus, and urinary, dyspeptic, and other diseases. On the other hand it has been asserted, that the lime salts thus introduced into the system are necessary to health and due development, and that those who drink soft water are deficient in stature and strength. The difficulty of obtaining statistical evidence on this question is manifestly very great, as the difference which might exist between the rates of mortality of two towns, having

water supplies differing in hardness, would be marked by greater differences arising from varying conditions of drainage, ventilation, density of population, &c. A large number of towns of all kinds scattered over Great Britain were tabulated according to the hardness of their water supplies. It was found that of twenty-six towns, each with an average population of 73,000, and supplied with water having less than 5 parts of hardness per 100,000 parts, the average annual mortality was 29·1 per 1000; of twenty-five towns, with an average population of 82,000, and a water of from 5 to 10 parts of hardness. it was 28·3; and of sixty towns, with an average population of 45,000, with water exceeding 10 parts of hardness, it was 24·3. This would indicate that hard water was most wholesome, while moderately hard and soft waters were comparatively unwholesome.

But all weight is taken from this conclusion, by the fact that of the sixty hard water towns thirty possessed the water closet system, while of the other fifty-one only six were so arranged, the pestiferous midden system being prevalent. Moreover, the latter had a population, on an average, nearly twice as large as the former, and therefore probably of greater density.

When the towns are classified according to their position, somewhat different results are obtained. Thus: of five seaport towns, with an average population of 163,000 supplied with soft water, the annual mortality per 1000 was 29·4; of three, with an average population of 226,000 supplied with moderately hard water, the rate was 32·1; and of six such towns, with an average population of 116,000 supplied with hard water, it was 25·1. This would indicate that moderately hard water was most unwholesome, which is absurd. The differences in the rate of mortality depend, doubtless, on other causes, such as density of population and nature of sanitary arrangements. In a similar way, taking inland manufacturing towns by themselves, soft water would appear most unwholesome, and hard water best; and from inland non-manufacturing towns, that moderately hard water was worst, and hard water best. A better prospect of success is presented by an examination of our health resorts. Here, from the absence of manufacturing operations, and the manifest interest of the authorities to obtain and preserve a thoroughly healthy condition, many causes which disturbed the previous comparisons are absent.

COMPARATIVE MORTALITY IN DISTRICTS CONTAINING SOME OF THE PRINCIPAL ENGLISH WATERING PLACES.

Nature of Water.	Number of Districts.	Average Population in 1871.	Mortality per 1000 per annum for the decade 1861–70.
Soft,	5	48,430	19·5
Moderately hard,	3	33,480	19·2
Hard,	12	53,170	20·4

This would tend to show that the hardness of water has little or no influence on health, and indeed the rate of mortality of the individual towns in the same hardness division varies more than the average rates of the three divisions shown above. While, therefore, waters of excessive hardness may possibly be injurious, it appears that, apart from these, waters of all degrees of hardness are equally wholesome if otherwise equally free from deleterious organic matters.

The Softening of Hard Water.—Hard water is unfit for washing, and for nearly all manufacturing purposes, but it may be softened by four different processes, viz.:—by distillation, by the action of carbonate of soda, by boiling, and by the addition of lime.

By Distillation.—This method is chiefly, if not solely, used for the preparation of fresh from salt water, for the supply of ships at sea. It is costly, but is the only process applicable under the circumstances. By it all fixed or non-volatile matters are entirely separated, as are also necessarily all organized bodies, so that such water may be used with absolute immunity from risk of infection, a fact of no small importance in unhealthy localities. When freshly prepared it has a vapid and unpleasant flavour, due partly to deficient aëration and partly to the presence of traces of volatile organic substances; both of these objections are removed by filtration through animal charcoal.

By the Action of Carbonate of Soda.—Carbonate of soda decomposes the bicarbonate and sulphate of lime and magnesia, to the presence of which the hardness of water is almost exclusively due, forming soluble bicarbonate and sulphate of soda, and insoluble carbonates of lime and magnesia. This action takes place slowly in the cold, and rapidly at a higher temperature. As the soda salts have an unpleasant taste, water thus softened cannot be used for drinking purposes. This method is commonly in use by laundresses, who thus avoid waste of soap. The first action of soap on hard water is to soften it, the soap taking the place of the carbonate of soda before mentioned; and it is only when this softening is complete that the detergent action of the soap can commence. Soap thus used is much more costly than carbonate of soda, a larger quantity being required; and its price being also much higher, the relative cost is about as 16 to 1.

By Boiling.—This method only applies to that part of the hardness of a water which is due to the presence of bicarbonates of lime, magnesia, and iron, but is not applicable to that arising from sulphates. When such water is boiled the bicarbonates are gradually decomposed, the insoluble carbonates being precipitated and carbonic acid expelled with the steam. Ebullition for about half an hour is sufficient. It is expensive, the cost not being much less than that of softening by soap; and it is troublesome, since the vessel in which the boiling is conducted becomes coated with a hard lining of carbonate of lime which is not easily detached, but, if allowed to accumulate, becomes a source of danger to the vessel in which it occurs. This process does not prevent the use of the water for drinking purposes.

By the Addition of Lime.—This process is applicable to the same kind of water as the preceding, and to

the same extent. Instead of removing the carbonic acid by boiling, it is rendered insoluble by the addition of lime, forming with the latter insoluble carbonate of lime, which is precipitated together with the carbonate of lime or magnesia resulting, as in the preceding process, from the decomposition of the soluble bicarbonate. Thus, while the bicarbonates are removed, nothing is added to the water, and it is suitable for all purposes. This method was devised by the late Dr. CLARK, Professor of Chemistry in the University of Aberdeen, and published by him about the year 1841.

To apply it on a small scale, about 1 oz. of quicklime is required to be added to each 700 gallons for each part of temporary hardness in 100,000 parts of water. The quicklime is slaked in a pailful of water, well stirred to form milk of lime, and then poured into the cistern, which should already contain at least 50 gallons of the water to be softened. Any coarse particles from the lime may be left in the pail. Fill the pail again with water, and stir and pour this also into the cistern. Then add the remainder of the 700 gallons. If the running of the water does not thoroughly stir up and uniformly mix the contents of the cistern, this must be done by means of a wooden or iron paddle. The water will appear very milky, and should be left at rest to deposit the precipitate. In about three hours it will be fit for washing, and in about twelve hours for drinking.

This process is now in use on a large scale in numerous places, being applied to the entire water supply of several towns. In such cases clear *lime water* is used in place of milk of lime, and thorough mixture is attained by running the hard water and the lime water into depositing tanks simultaneously in streams suitably proportioned. The time required for subsidence is reduced by the use of telescopic discharge pipes, by means of which the clear water is constantly taken from the surface, the overflow pipe being lowered as the water runs off. The quantity of lime water employed is controlled by occasionally testing in a porcelain cup with a solution of nitrate of silver. If the lime be in excess, a brown colour is produced; but when the proper proportion only is present, a very faint yellow is seen on adding the nitrate of silver. The cost of softening by lime is very small; 1,000,000 gallons of water, with a temporary hardness of 20 parts per 100,000, could be softened at a cost for lime and labour of about 23*s*. The carbonate deposited for the most part carries down with it a large part of the organic colouring matter in the water, so that after subsidence the clear water generally exhibits, when seen in a large bulk, a magnificent blue tint, a very important improvement being thus produced in the character of the water, as is shown in the accompanying table. The result in the case of the Thames water would probably have been still better, had not the softened water been necessarily exposed in a cistern on the roof of a house to a London atmosphere for twenty-four hours.

Description.	Total Solid Matters.	Organic Carbon.	Organic Nitrogen.	Hardness.
Caterham water supply, before softening, February 14, 1873.....	27·68	·028	·009	21·2
Ditto. after softening, ...	8·80	·015	·003	4·4
Thames water, supplied by Grand Junction Co., before softening, average of 9 experiments in 1870–71,	27·85	·161	·026	20·8
Ditto, after softening, .. .	12·85	·122	·022	5·1
Lea water, supplied by New River Co., February 14, 1871,.....	30·60	·135	·018	22·4
Ditto, after softening, ...	13·76	·100	·011	6·0

The system is now in active operation, on the large scale, at the Chiltern Hills Water Works, at Caterham, at Canterbury, and at Bushey.

ON THE FILTRATION OF WATER.—The most obvious result of the filtration of water is the removal of suspended matter, so that a turbid water becomes bright and clear. Its efficiency in this respect depends chiefly on the closeness of texture of the filtering medium, *i.e.*, the smaller the interstices through which the water has to pass the more efficient will be the purification. Very finely divided suspended matter, such as clay, requires a very fine filter, and also that the passage of the water should be slow. The efficiency of a filter is often judged solely by its clarifying action, and when the water is passed rapidly through a thin filtering medium, *e.g.*, a paper filter, there is probably little if any other result. When, however, the stratum of filtering material is of considerable thickness, and the rate of filtration slow, an important reduction in the quantity of organic matter present in solution may be effected in addition to the removal of suspended matter. The organic matter is oxidised by the oxygen dissolved in the water, supplemented perhaps in some cases by oxygen supplied by the nitrates present. It is desirable, therefore, that the water to be filtered should be well aërated, and, if practicable, that the filter itself should from time to time also be aërated. The importance of this was seen in some experiments made on the filtration of sewage through various materials. The sewage itself probably contained no oxygen in solution, and certainly did not contain sufficient for the destruction of the organic matter in solution. It was found that when it was passed unintermittently through a thick sand filter, at first considerable oxidation took place, but this soon ceased, and the filter speedily became choked; but when the sewage was supplied intermittently, so that the filter was well aërated after each charge, the action could be continued indefinitely if the amount of organic matter in each charge was not too great for the amount of atmospheric oxygen introduced at each interval. When the charge was increased beyond this, the purification ceased, and the filter speedily became choked. If the quantity of oxygen is sufficient, the degree of purification will depend on the nature of the filtering medium, its state of division,

and the length of time during which the water is in contact with it.

In the following table are shown the results of filtration through sand, animal charcoal, and spongy iron:—

RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

Description.	Total Solid Matters.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Previous Sewage Contamination.	Chlorine.	Hardness.			Remarks.
									Temporary.	Permanent.	Total.	
New River Company's water at Stoke Newington, before filtration,	31·98	·350	·084	·004	·310	·397	2·810	1·70	16·4	6·6	23·0	Turbid.
After filtration through sand,	30·16	·246	·042	—	·310	·352	2·780	1·65	16·4	6·6	23·0	Clear.
Grand Junction Company's water before filtration,	24·60	·129	·023	—	·188	·211	1·560	1·60	—	—	19·4	——
After filtration through fresh animal charcoal,	19·40	·029	·007	·013	·194	·212	1·730	1·60	—	—	15·2	——
Grand Junction Company's water before filtration	28·36	·380	·074	·001	·265	·340	2·340	1·65	—	—	18·0	——
After filtration through spongy iron,	14·70	·038	·012	·010	·128	·148	1·040	1·70	—	—	8·1	——

The filtration of water through sand, as usually applied for town supplies, is for the most part primarily directed to the removal of mechanically suspended particles; but it usually has also at least a slight effect in removing organic matter. In the example given above of the New River Company's water, nearly 30 per cent. of the organic carbon and one-half of the organic nitrogen were removed. That company filters the water at a very slow rate through filter beds of considerable thickness; in some other cases, where a greater velocity is adopted, the improvement is much less.

Filtration through animal charcoal is more energetic. In the example given above the filter used was a small domestic one, through which the whole of the water supplying a family of nine persons was passed. In this case the organic carbon was reduced to about one-fourth, and the organic nitrogen to about one-third of the original proportion, and the mineral matter was also considerably reduced. This last action ceases after a week or so, but the removal of organic matter continues in a diminishing ratio for some months. If the filter is much used, the filtering material should be renewed every three months, or more frequently if an impure water is used; otherwise small worm-like organisms are developed in the charcoal and pass out with the filtered water.

The action of spongy iron, obtained by reducing hæmatite by carbon at the lowest practicable temperature, so that the metallic iron may remain in a finely divided state, is still more energetic and persistent. The numbers given in the above table indicate a very great improvement; the total solid matters being reduced to about one-half, the organic carbon to one-tenth, the organic nitrogen to less than one-sixth, and the hardness to less than one-half. This continued for upwards of twelve months, and exhibited no signs of exhaustion. This form of filter was introduced by Professor GUSTAV BISCHOF, who has shown that all putrefactive germs and organisms are destroyed by passage through a spongy iron filter.

Although such good results *can* be obtained by the use of domestic filters, it is only when great care is exercised. If the filtering material is not renewed when required, and the filter properly protected from impurities, water is often actually injured by passing through a dirty filter. It is better to use the water of the ordinary town supply, taken direct from the main, or from a cistern properly protected and periodically cleaned, than to pass it through a neglected filter. In this respect the spongy iron filters possess the advantage that, when exhausted, they no longer allow the water to pass through them.

WINE.—*Vin*, French; *wein*, German.—A spirituous liquid prepared from the juice of grapes by fermentation. Grapes are the fruit of many varieties of vines, of which about 600 are cultivated, while a number, not amounting to 100, are known to occur as wild plants indigenous to various countries. It is probable that the vines cultivated in various localities to which they are best adapted, are derived from vines which were indigenous to that locality. Not all grapes are eatable, and not all grapes yield good wine. Thus, an American wild vine produces small acid black grapes which cause a burning sensation and a swelling of the lips in persons partaking of them, from the presence in the husk of an acid substance. Grapes which are good for wine-making are frequently not suitable for eating, and the best grapes for eating give inferior or bad wine.

Mineral Constituents of the Vine.—The ash of the vine consists of a part which is soluble in water, and of another which is insoluble. The soluble part comprises the alkali metals, potassium and sodium, combined with carbonic acid, sulphuric acid, and chlorine; while the insoluble part contains calcium, magnesium, iron, and manganese, combined with carbonic, phosphoric, and silicic acid. The proportions in the ash of the vine of alkalies to earths are about equal; and again, the united weight of these bases is about equal to the weight of the half of the entire ash. Different vines yield different proportions of ash; but vines of the same kind, in full development and at the same period of

vegetation, yield very similar proportions of ash. The ripe woody canes of one year's growth contain from one-fourth to one-fifth of their weight of moisture, or 25 to 20 per cent., and from 2·2 to 4·2 per cent. of ash. The leaves yield the greatest amount of ash, and the old wood and the ripe grapes the smallest. The less mineral matter any part contains, the greater is in that ash the proportion of soluble salts. The leaves and wood are rich in potassium salts, while the bark contains much calcium carbonate. The pith and stones (seeds) are rich in calcic phosphate. The ash of the canes, of the murk, and of a litre of wine, from one and the same vine, have yielded the following quantities of ingredients:—

Elements contained in the Ash.	Ash of Canes in per cents.	Ash of Murk in per cents.	Ash of 1 litre of Wine in grams.
Potash,	18·0	36·9	0·842
Soda,	0·2	0·4	—
Lime,	27·3	10·7	0·092
Magnesia,	6·1	2·2	0·172
Ferric and aluminic oxide,	3·8	3·4	—
Phosphoric acid,	10·4	10·7	0·412
Sulphuric acid,	1·6	5·4	0·096
Chlorine,	0·1	0·4	traces.
Carbonic acid	20·3	12·4	0·250
Sand and little silica,	10·9	15·3	0·006
Loss,	1·3	2·2	—
Totals	100·0	100·0	1·870

In the same case the canes gave 2·44 per cent. of had given 1·870 gram. of ash, or 0·19 per cent.; ash, and the murk, air-dry, 6·65; 1 litre of wine the density of the wine being about 0·960. It is therefore evident that the ash of the canes contains less potash and more lime than that of the murk, and that the proportion of potash to lime is highest in the ash of the wine. Thus we have per cent. of potash contained in ash of canes 18·0, murk 36·9, wine 45·0; per cent. of lime contained in ash of canes 27·3, murk 10·7, wine 4·9. But the relations of magnesia in those parts are different from those of potash and lime, for the percentage of magnesia in ash of canes is 6·1, murk 2·2, wine 9·2. The wine yields a very small percentage of ash compared with the other parts, and in consequence its percentage of alkalies is smaller than that of any other part of the vine; but as it has lost much mineral matter during fermentation, the quantity of its ash is not the measure of the quantity of mineral matter removed by it from the soil: for this estimation the grapes or murk and juice combined before fermentation have to be examined. Grape-bunches contain about 4 per cent. of stalks, 22 per cent. of husks, seeds, and insoluble matter, and 74 per cent. of juice. In 100 parts of bunch there are 2·194 parts of ash, of which about 1·431 is in the stalks, 0·5 in the murk, and 0·263 in the filtered juice. These relations vary with the years and the varieties of grapes; but the proportion of the ash in the several parts is least changeable. The ash of must contains from 62 to 72 per cent. of potash, oda 0·3 to 2·6, lime 3·3 to 5·2, magnesia 3·2 to 4·7, erric oxide 0·09 to 0·72, manganic oxide 0·09 to 0·82, sulphuric acid 3·6 to 5·5, chlorine 0·47 to 1·10, silica 1·1 to 2·1, phosphoric acid 14·0 to 17·0 per cent. There is no particular difference between the ash of unripe and ripe grapes.

Organic Ingredients and Chemical Development of the Vine.—The seed of the vine contains lignine, starch, tannic acid, fatty oil, several phosphorized and albuminous substances, and the mineral salts already referred to, in which phosphoric acid and potash predominate. From these the young plant is at first supplied, until it begins to take up nourishment by the roots from the soil, and by the leaves from the air. The assimilated matters are inorganic; namely, carbonic acid, ammonia, and water, and the mineral salts already described. The specific process of vegetable growth under the influence of light and heat eliminates oxygen from the carbonic acid, and combines with the more carbonized products the elements of water. This product, oxalic acid, combines with some of the bases; then by the combination of two of its particles and the substitution of some oxygen by hydrogen, malic acid, the acid also contained in apples, is formed. This malic acid, by a slight addition of oxygen, is easily transformed into tartaric acid. Tartaric acid, again, by the union of three of its particles, and the addition of hydrogen from decomposed water, may easily be transformed into grape-sugar, or similar carbohydrates, cellulose, cane sugar, gum, and starch. The nitrogenized ingredients of the vine are derived from ammonia by substitution of its hydrogen by more complicated radicals—methyle, for example; trimethylamine exists in wine. On entering into combination with complicated carbonized matters the ammonia loses much of its character as an alkali, and produces a series of alkaloids, which then by further development and combination produce the albuminous and phosphorized substances.

The sap rises in the canes at the beginning of spring, and when flowing from cut surfaces, is termed *tears*, and the process of its flowing, *weeping* of the vine. One litre of sap leaves about 2·5 grams. residue, of which 1·9 are organic, with tartaric acid, gum, and starch; the inorganic, 0·6 gram., contain lime, potash, a trace of phosphoric acid, and some ammonia. The rising of the sap takes place with great force, which has been measured by various observers and found to equal the pressure of a column of water 21 feet, or of a column of mercury 22 inches in height.

The young shoots of the vine contain acid tartrate of potash in much larger quantity than the sap; cellulose in constantly increasing quantity, and the mineral constituents, already mentioned, are deposited within their structure and that of the leaves. In the expressed juice of *entire branches* there are found *vegetable fibrine*, which is deposited with the *chlorophyll* as a green precipitate; *vegetable albumen*, which is precipitated by boiling; *tannin*, recognized by its reaction with ferric salts and gelatine; *acid tartrates of potash and lime*, which can be obtained by evaporation and crystallization; *starch*, *gum*, and *mineral salts*. The part remaining insoluble consists

mainly of *lignine* or *cellulose;* of this substance all wood, old and young, is composed. In the cell-cavities of the wood there is deposited in autumn a quantity of starch. The *tendrils* contain malates and tartrates, little *tannin*, and have a taste of unripe fruit.

The *grapes* contain in their unripe state *malates* and *tartrates*, mainly of potassium, which vary in proportion, according to the period of development. Before the appearance of any sugar malates prevail; when the grapes become sugary tartrates prevail, which in the fully ripe grapes maintain their preponderance. The grapes then also contain fibrine, albumen, gum, pectin, tannin, and in largest quantity the sugar peculiar to fruit; the tannin is not in solution in the juice, but deposited in the husk and seed, and requires maceration for its extraction. The husk of the blue and black grapes contains the *blue colouring matter* also deposited in the insoluble state along with the tannin, and extractable only by alcohol and acid, or wine. The stalks contain starch during summer, but lose it towards autumn; and when the grapes are ripe they contain tannin. The amount of acid in the grapes increases during their growth, and decreases again during ripening. When the juice from grapes of various periods of growth simply is considered, without reference to the number and weight of the berries, it is observed to become steadily less and less acid, the decrease being, between extremes, from 35 *pro mille* in the middle of August to 7 *pro mille* at the end of the vegetative period in the first days of November. This change is completed before the middle of September in the grapes growing in southern climates.

Relation of acid and sugar in grapes during ripening.—The percentage of free acid present in grape juice diminishes with the increasing ripeness of the grape, while the percentage of sugar increases at the same time considerably. As the weight of the fruit augments considerably during the process of growth, the total amount of free acid present in the ripe grape may be actually greater than in the unripe fruit, and yet its proportion per cent. be considerably diminished. The acid may increase during ripening absolutely, but is necessarily diminished relatively to the proportion of other ingredients which are formed massively during ripening, particularly sugar. Therefore the proportions of acid in unripe and ripe grapes affords no evidence regarding the question whether or not during the progress of ripening acid is transformed into sugar. In some French black grapes peculiar processes of ripening are observed—one, which is peculiar to the grape which is not yet black, consisting in an augmentation of sugar; the other, a process mostly accomplished in the black grape, consisting in a diminution of acidity.

Vintage and Vinification.—The grapes should be gathered when they are ripe. In many parts of the south of Europe it is considered that the grapes are ripe when they have attained their greatest volume, and they are then vintaged. In some of the most celebrated vineyards for the production of white wine the grapes are allowed to hang until they attain the maximum of sweetness and maturity, and are commencing to decay or pass into the state of sweet-rot (Sauterne; Rhinegau; Vouvray). In this manner highly flavoured or sweet wines are produced, the latter owing their sweetness mainly or in part to the presence of unfermentable *inosite*, the sugar peculiar to brain and muscles. In dry and hot climates the grapes are also allowed in part or whole to passulate, *i.e.*, to be transformed into raisins while hanging on the vine; and with the aid of these sweet, thick, syrupy wines are made, either mixed with alcohol, as the Malaga, or not mixed with alcohol, like Tokay and Rota. The red or black grapes are vintaged at certain stages of maturity, which are known to produce a certain amount and kind of red colour in the wine; this is shortly after the stage of greatest volume, and before that of beginning passulation. The latter process destroys the blue colouring matter, so that—*e.g.*, in Rota Tent, entirely made from black grapes—no red colour is distinguishable. In the Champagne the black grapes of the pineau are gathered at the time of their greatest volume, because when a little over-ripe they yield a slightly coloured juice (partridge eye), which is objected to by traders.

Modes of Vintage.—The most common mode of vintage consists in cutting off all the grapes and carrying them to the press. The bunches should be cleaned from impurities, unripe and putrid berries. The white grapes are in most countries pressed without previous separation of the stalks; they are also but rarely fermented together with stalks and husks, *e.g.*, in Portugal. The black grapes are mostly fermented with husks and stalks, as in Portugal, Spain, south of France, Gironde, and Burgundy; in some parts only, and always exceptionally, the stalks are removed from the grapes by hand or machines (French, *égrappage*).

Mashing and Crushing.—The grapes are most commonly crushed by being trodden by men; in other parts they are crushed by machines (grape-mills), consisting of grooved wooden rollers working against each other. In the preparation of Champagne the grapes are not crushed in detail previous to their being put into the press, and the only crushing which they receive is by the press itself. It is for this reason that the presses in the Champagne are the most powerful of any known. The presses are of two kinds—screw-presses and beam-presses. The varieties of screw-presses are so numerous that an enumeration of them and a description of their differences becomes impracticable. In the beam-presses the power is produced by weights attached to the end of a long beam acting as a lever; but with them also the weights at the end of the beam are mostly lifted, and therefore made active by screws passing through the free end of the beams (Alto Douro).

Fermentation.—White wine is generally fermented in barrels, with the ordinary bunghole at the top open for the escape of the carbonic acid gas. But valuable red wines are fermented in vats, *i.e.*, conical wooden casks, open at the top. This is a mechanical

necessity, owing to the complications introduced into the preparation of red wine by the bulk of the husks, and the necessity for stirring. Port wine (Alto Douro) is fermented in low receptacles of stone or masonry (*lagares*), in which the grapes are also trodden, and after fermentation pressed. The common red wines of the south of France and centre of Spain are fermented in cisterns of masonry lined with plaster of Paris, which alters the wines in a definite manner, to be considered below. When the wine has completed its fermentation and become clear, the yeast and impurity are deposited in the bottom of the cask. From this deposit the wine is separated by decantation, a process termed *racking*. This is repeated from time to time, but is rarely by itself sufficient to make the wine quite clear. The wines are therefore clarified (fined) by various means. Delicate white wines are mostly fined with isinglass, which is softened in water or wine, and then stirred up (roused) with the wine to be fined. Brandied white wines, such as sherry, are mostly fined with white of egg, and the coarse varieties with skimmed milk. Spanish earth, so-called, and other varieties of clay, including Chinese, are also used to fine wines. In all these cases a precipitate is produced, which envelopes and drags down the fine particles which of themselves have not sufficient gravity to sink in the liquid.

Petiot's Process of making sugar-water wines.—The husks of grapes freed from their primary juice will cause fermentation in sugar solution, and produce a fermented liquid not unlike wine.

Gall's Process of improving acid wines.—In cold climates and years the grapes sometimes remain acid, and the wine resulting from them would be undrinkable if not freed from its acid in some manner: this used to be effected with chalk. Gall, however, introduced into the wine cellars of the Moselle the practice by which home-made wines are commonly made in England, namely, diluting the acid fruit-juice with water, and then adding sufficient sugar to yield a desirable amount of alcohol after fermentation. These processes of Petiot and Gall are used for increasing the quantity of cheap beverage, even from grapes from which wines could not be obtained fit for commerce or transport. In the process of Gall, or in the processes of making British fruit-wines, the mixture of fruit-juice, water and sugar should be so made that it contains five *pro mille* of acid expressed as tartaric, and 20 per cent. of sugar.

Plastering of Must and Wine.—In the south of France, in the departments bordering upon the Mediterranean, and in Spain, plaster of Paris is dusted over the grapes, added to the grape-juice, or even placed into the barrels with the ready-made wine; in these parts, also, wines, particularly red wines, are fermented in cisterns of masonry covered inside with a layer of plaster of Paris. The gypsum decomposes the tartrate of potassium present in the juice, insoluble tartrate of calcium being formed, and sulphate of potassium going into solution. As the sulphate of potassium is much more soluble in wine than the tartrate, such plastered wine has always a peculiar mineral taste, and not rarely, and particularly in delicate persons, acts as a purgative, and on continued use deranges the action of the heart. The grounds of this practice of plastering must and wine cannot be learned even by inquiry in the localities where it is employed; it seems to be a mere traditional empiricism.

Alcohol.—The general chemistry of alcohol is described in the article relating to that substance. We here confine ourselves to the consideration of alcohol as far as it affects the nature and effects of wine, and the estimation of its quantity by methods specially applicable to wine.

Distillation.—The quantity of wine used for the experiment should amount to from 200 to 300 c.c. It may be weighed, in which case the experiment becomes independent of temperature; or it may be measured, when the temperature of the sample has to be ascertained. The weighed or measured quantity of wine is poured into a flask or retort, rendered slightly alkaline by caustic soda, mixed with a small quantity of tannin to prevent frothing, and then carefully distilled by driving the alcoholic vapour into a condenser by means of heat. It is well to distil from one-half to two-thirds of the liquid in the flask. Strong and heavy, *i.e.*, sugary wines, may advantageously be diluted with water before distillation. As soon as the necessary quantity is distilled, the distillate is mixed with so much water as may be required to raise it to the exact weight or measure of the wine originally taken for distillation. The mixture must be well agitated to effect complete homogeneity. Its specific gravity is next taken. This may be done by means of the hydrometer, or by means of the specific gravity bottle and balance. The specific gravity bottle should contain from 20 to 60 c.c. The temperature of its contents has to be carefully noted. It is convenient so to manage the experiment that the fluid has the temperature of 15°·5 C., for which most alcohol tables are constructed; and in case it should be either higher or lower, to cool it down or raise it up to the desired point. For variations of temperature, which are not far removed from the standard calculated, corrections may be applied without much trouble. The amount of such correction for each degree Centigrade varies considerably with the strength of the spirit, and though very slightly, with the glass of which the specific gravity bottle is made. In cases where the temperature differs only a few degrees either way from the mean, this correction can be applied with sufficient accuracy by means of the formula—

$$D = D' + d\left(0{\cdot}00014 + \frac{1 - D'}{150}\right)$$

D is the required density at 15°·5, D′ the density observed, and d the difference between 15°·5 and the temperature at which D′ was taken. If this was below 15°·5 the — sign is used; if above, the + sign; 0·00014 is the correction per degree Centigrade with distilled water; the fraction $\frac{1 - D}{150}$ gives

approximately the additional correction for a spirit of the observed specific gravity D′.

For D thus calculated the corresponding alcoholic strength may be found in the proper tables; and this strength, as regards the wine, may be expressed essentially in three different ways:—first, in per cent. by volume in volume of wine; secondly, in per cent. by weight in weight of wine; and thirdly, in per cent. by weight in volume of wine. The alcoholic strength of the distillate will sometimes directly represent the strength of the wine, according to one or other of the above ways of expressing it; sometimes an additional calculation is necessary before the desired result is obtained.

In case the wine and distillate have been measured, and we require—

1. *Per cent. by volume in volume of wine*, then the alcoholic strength of the distillate, as given by the tables, showing per cent. by volume, will at once give the desired result; the strength of distillate and wine as thus expressed being identical.

2. *Per cent. by weight in weight of wine*, then the alcoholic strength of the distillate, according to the table giving per cent. by weight, is multiplied by the specific gravity of this distillate and divided by the specific gravity of the wine.

3. *Per cent. by weight in volume of wine.* The percentage by weight of the distillate is multiplied by the specific gravity of such distillate.

In case the wine and distillate have been weighed, and we require—

1. *Per cent. by volume in volume of wine*, then the percentage by volume of the distillate is multiplied by the specific gravity of the wine, and divided by the specific gravity of the distillate.

2. *Per cent. by weight in weight of wine.* These are at once given by the percentage by weight of the distillate.

3. *Per cent. by weight in volume of wine.* The percentage by weight of the distillate is multiplied by the specific gravity of the wine.

In case the wine has been measured and the distillate weighed, the percentage by weight of the distillate will give at once per cent. by weight in volume of wine.

The method of expressing the alcoholic strength of a wine in per cent. by weight in volume is the one most commonly adopted in scientific works on the subject, and seems preferable to every other. If in this case the decimal point is moved one figure to the right, the number of grammes of alcohol contained in 1 litre of wine is obtained; and if this latter figure is further multiplied by seven, the number of grammes of absolute alcohol in 1 gallon (six bottles) of wine is given.

The English Excise Office has adopted a method of giving the alcoholic strength of wines or spirits differing from all the foregoing, viz., in volume per cent. of *proof spirit*, indicated as degrees by SYKE'S hydrometer. These are indicated directly by the specific gravity of the distillate, taken by balance or hydrometer, in case both wine and distillate have been measured. By an Act of Parliament which was passed in the fifty-sixth year of the reign of GEORGE III., chapter 160, in the year 1816, it is enacted that the standard of all spirits upon which the Excise shall levy taxes is to be a mixture of alcohol and water which shall weigh 12, while the same volume of distilled water shall weigh 13, all at a temperature of 51° Fahr.; or in the words of the Act, "And whereas, since the passing of the said Acts, an hydrometer, called SYKE'S hydrometer, has with great care been completed, and has, by proper experiments made for that purpose, been ascertained to denote as proof spirit that (mixture of spirit and water) which at the temperature of 51 degrees by Fahrenheit's thermometer weighs exactly $\frac{12}{13}$ parts of an equal measure of distilled water," &c.

The standard of proof spirit no doubt was originally obtained from the average strength of brandy distilled from wine by a simple still. Before science was applied to the estimation of the strength of such spirit, it used to be tested in the following manner:—Some gunpowder was put into a saucer, and some of the spirit to be tested was poured over it; then the spirit was set fire to and burned, and at the conclusion of the combustion it was observed whether or not and to what extent the gunpowder also took fire. The spirit was called "proof" if it was sufficiently concentrated to cause the gunpowder to burn; but if the spirit contained so much water that at the end of the combustion the gunpowder was wet, then it did not burn, and was not "proof." It is to be hoped that in the progress of time Great Britain will abandon this standard of proof spirit, and adopt the one now used amongst all continental nations, namely, the standard of absolute alcohol.

Determination of the Alcohol by Indirect Means.—The method of TABARIE, which was after him much used and recommended by BALLING and MULDER, is based upon the fact that the presence of a certain amount of alcohol in a mixture will depress its specific gravity below what it would be if the alcohol contained in it were replaced by an equal proportion of water, and this depression will always be effected whether the mixture consists of water and alcohol only, or contains other substances in solution at the same time. If then, knowing the specific gravity of such a mixture, we expel the alcohol and replace it by water, and again take the specific gravity, we may calculate the specific gravity of a spirit containing the same percentage of alcohol as the mixture with the help of the equation $D' : D = 1000 : X.$, where D′ is the specific gravity of the mixture deprived of alcohol, D the specific gravity of the mixture with the alcohol in it. The experiment is best performed by TABARIE'S original process of measuring the wine, and bringing the evaporated wine to the same measure by the addition of water. BALLING determines the difference by bringing the evaporated wine to the same weight as the wine taken, by the addition of water.

Alcohol Estimations Based upon the Boiling Points of Alcoholic Mixture.—These estimations are carried out by special instruments, termed *ebullioscopes;* amongst these the instruments constructed by BROSSARD,

POHL, VIDAL, URE, CONATZ, and CROCKFORD, are best known. They are, however, not very certain in their action, and liable to give misleading results.

Alcohol Estimation Based upon the Vapour Tension of Alcoholic Liquids. Geisler's Vaporimeter.—The action of this instrument is based upon the circumstance, that the tension of the vapour of a mixture of pure alcohol and water at the temperature of 100° rises with the alcoholic strength. Applied to wine, the vaporimeter indicates quantities of alcohol which are sometimes above, sometimes below, those found by distillation.

Alcohol Estimation Based upon the Expansibility of Alcoholic Mixture by Heat.—SILBERMANN has applied this principle to an instrument termed the *dilatometer*. With wines which are not too strong, and do not contain more than 5 per cent. of extractives, this method gives tolerably accurate results; to strong wines, with much solid matter, it is inapplicable.

Acet-Aldehyde.—The presence of aldehyde in wine is a decided mark of unsoundness; it is easily detected by its peculiar smell and flavour. If such a wine be neutralized by an alkali, and submitted to distillation through a well-cooled condenser, the aldehyde may be readily detected in the first portion of the distillate by its smell, flavour, its reducing action upon silver salts, and by its easy conversion into acetic acid.

VINOUS ACIDS.—The acids hitherto distinctly recognized as present in wine are of two kinds, namely, those originally present in the grape, as tartaric, malic, and tannic; and those produced during fermentation, as acetic, formic, succinic, carbonic, and traces of the higher members of the fatty acid series, as propionic, butyric, and particularly œnanthic acid.

Tartaric Acid ($C_4H_6O_6$).—Tartaric acid occurs in wine in two varieties, namely, as dextro-tartaric acid, and as racemic acid; levo-tartaric acid as such does not occur in wine. Most of the acid is combined, as acid potassium salt, so called tartar ($KH,C_4H_4O_6$). Plastered wines, such as sherries, contain no tartaric acid, but sulphuric instead. The acid tartaric ether ($C_2H_5,H,C_4H_4O_6$) also occurs in wine.

Malic Acid ($C_4H_6O_5$) occurs in must and wine free and in combination. Like tartaric, it is dibasic, forming two classes of salts and ethers, acid and neutral. As its lime-salt is soluble in water, it is not removed to any very great extent from grape-juice by the process of plastering.

Succinic Acid ($C_4H_6O_4$) is produced during the fermentation of grape-sugar, to the extent of about a half per cent. of the quantity of sugar decomposed. It is therefore always found in small quantity in wine. It may be extracted from the residue of wine by a mixture of 1 part of absolute alcohol and 2½ parts of ether; from the condensed extract the succinic acid, after neutralization, may be precipitated as ferric salt; or after neutralization with lime-water, as calcium salt by a mixture of ether and alcohol. One litre of wine contains from 1 to 1·5 gram. of succinic acid.

Acetic Acid, $C_2H_4O_2$, is found in all wine in small quantity, varying between 0·5 and 1·5 per thousand. Must, after partial fermentation, contains many of the elements favourable to the production of vinegar by the oxidation of alcohol. Where the must ferments in open vats it exposes a large surface to the atmosphere, which is further increased by the thick froth covering it, or as is often the case with red wines, by the skins and stalks of the grapes which float on the top. The formation of vinegar by the oxidation of alcohol is prevented by fermentation in closed vats; or the effect of such formation of vinegar in the husks of red wine is obviated by the removal of that part of the top (*chapeau*, in French,) which smells of vinegar. A second source of acetic acid in wine, and one which appears to be much more dangerous than the oxidation of alcohol, is the slow fermentation of malic acid (and, perhaps, of tartaric acid also), under the influence or in the presence of an organized ferment, which, when present in the mycodermatous state, produces the condition of wine known as ropiness or viscosity. Under these circumstances, malic acid may, perhaps, split up according to the formula—

$$\underset{\text{Malic Acid.}}{3(C_4H_6O_5)} = \underset{\text{Succinic Acid.}}{2(C_4H_6O_4)} + \underset{\text{Acetic Acid.}}{C_2H_4O_2} + 2(CO_2) + H_2O.$$

By this process there is just sufficient acetic acid formed to spoil the wine; the only certain means of preventing this danger is the heating of the wine, as recommended by PASTEUR.

The volatile acid of wine is almost entirely composed of acetic acid, as can be proved by combining the distillate from wine with baryta, and determining the atomic weight of the product. German wines contain the minimum of acetic acid, from 0·36 per thousand to 1·78 per thousand. Greek wines contain the maximum amongst wines met with in trade, namely, between 1·53 and 3·63 per thousand.

Besides acetic, small traces of *formic acid* (CH_2O_2) are sometimes found in wine. The distillate, after neutralization and evaporation, is tested in the manner usual for formic acid, by nitrate of silver, or mercurous nitrate and heating.

The acids higher than acetic can only be obtained from large quantities of wine, by subjecting the united volatile acids to a process of fractional liberation and distillation; the first fraction contains the higher acids, the middle portions the acetic, the last portion the formic.

Œnanthic Acid, $C_{14}H_{26}O_3$, was discovered by LIEBIG and PELOUZE in the ether to which wine owes its characteristic vinous smell. It is obtained by boiling œnanthic ether with a solution of caustic potash, whereby alcohol is driven off and œnanthate of potassium is produced. When all the alcohol has been expelled by boiling the solution is acidified with dilute sulphuric acid, the oil which separates is washed thoroughly with hot water, and finally dried *in vacuo* over oil of vitriol. The pure concentrated acid thus obtained constitutes a soft, white solid, which melts at a little over 13° C., into a tasteless,

inodorous oil, soluble in alcohol and ether, but insoluble in water. It has a feeble acid reaction, and is readily soluble in caustic alkalies and alkaline carbonates, with formation of the salts of these bases. The acid is dibasic, and forms two kinds of salts, acid and neutral. When distilled by itself it breaks up into water and *œnanthic anhydride*, $C_{14}H_{24}O_2$; the latter boils at 260°, but decomposes in part, so that the boiling-point rises to 293°; the distillate becomes solid at 31° C.

Estimation of the Quantity of Acids in Wine.—The volatile acids may be conveniently estimated as acetic acid; the fixed acids may be estimated as if they were malic and tartaric only. The total saturating power is determined in 20 c.c. of wine by a standard solution of caustic soda of decinormal strength, logwood tincture being used as the indicator. Another 20 c.c. are then evaporated to dryness and heated for half an hour, until all volatile acid has been driven off, and the loss of water is restored. In this fluid the amount of fixed acid is now estimated; it represents the total free fixed acid of the wine, and the difference between this and the first estimation gives the total volatile acids present, as measured by their neutralizing power. The free volatile acid cannot be determined by distillation, as it does not completely pass over.

In good sound wines the total amount of free acid ranges from 0·3 to 0·7 per cent.; wines with more than the latter amount of free acid are neither pleasant nor wholesome. Of the total acidity not more than about 0·15 per cent. should be due to volatile acid.

Estimation of Tartaric Acid and Bitartrate of Potash in Wine.—The bitartrate of potash is slightly soluble in water, and insoluble in strong alcohol or a mixture of alcohol and ether. Upon this insolubility the methods for the estimation of tartaric acid and bitartrate have been based. According to Berthelot, 20 c.c. of wine are mixed in a stoppered bottle with 100 c.c. of a mixture of equal volumes of alcohol and ether; to another 20 c.c. of the wine a quantity of potash (sufficient to neutralize about one-fifth of the free acid of the wine) is added, together with 100 c.c. of the ether and alcohol mixture. Both bottles are then set aside for three days in a cool place; at the end of this time almost all the bitartrate of potash present in both bottles will have been deposited, sometimes in defined crystals. These precipitates are then collected on filters, washed with alcohol ether introduced with the paper into a flask each, and dissolved in distilled water, if necessary with the aid of heat. The free acid present in these solutions is then estimated by a decinormal solution of soda, with logwood as indicator.

The ether-alcohol retains only 0·004 gram. of bitartrate in solution; these have to be added to the quantities found. With this correction, the precipitate from the first 20 c.c. represents the bitartrate present in the wine; the precipitate from the second 20 c.c. contains the whole amount of tartaric acid present. In order to obtain the percentage of bitartrate and of tartaric acid in the wine, multiply the number of c.c. of decinormal soda required to neutralize the precipitates, *plus* the necessary correction of 0·21 c.c. for the bitartrate remaining in solution, by 0·094 and 0·075 respectively. The method of Nessler is similar to, but less accurate than the one described.

In the majority of wines all the tartaric is present as bitartrate; that is to say, there is a sufficient amount of potash present to enable the whole of the tartaric acid to be precipitated in this form by ether-alcohol. The wines, in fact, frequently represent a solution of bitartrate, saturated at the lowest temperature to which the wine may have been exposed.

All pure natural wine contains more or less of tartaric acid, and the quantity is probably the higher the riper were the grapes from which it was produced. There is not, however, any apparent connection between the amount of tartaric acid present and the quality of the wine. On the other hand, strongly fortified wines contain little or no tartaric acid, and this acid is almost entirely absent from all wines during the production of which *plaster of Paris* has been employed.

The amount of tartaric acid in wine is only a fraction of the entire amount of free fixed acid present in it; the greater part of the free fixed acid consists of *malic acid*. This can be determined by adding to, say 50 c.c. of wine, limewater as long as a precipitate is produced; this being filtered off, the filtrate is evaporated to 25 c.c., and mixed with much absolute alcohol. Malate and sulphate of calcium are precipitated, collected, dried, and weighed. The sulphate of calcium is then estimated and deducted from the total, leaving the malate of calcium. The other organic acids contained in wine cannot at present be estimated quantitatively with any degree of exactness.

Vinous Ethers.—By far the greater part of the volatile ethers found in wine is aceto-ethylic ether, $C_2H_3(C_2H_5)O_2$, which being volatile, and possessing a very decided smell, doubtless contributes much to the general flavour of the wine; but neither the characteristic wine-flavour nor the peculiar bouquet of wines is due to it. In wine the ether is formed by the action of acetic acid on alcohol, perhaps facilitated by the presence of other acids, but kept within certain limits by the presence of water. As the formation of a compound ether under these conditions takes place gradually, the amount of it present at a given time is, to a certain extent, a measure of the age of the wine. Besides acetic ether minute quantities of ethyl-compounds of the higher acids of the fatty series are present in wine, and contribute to its flavour.

Œnanthic Ether, $C_{18}H_{36}O_3$. Towards the end of the distillation of wine (or wine-yeast) an oily liquid passes over in small quantity, 40,000 parts of wine yielding about 1 part of the oil. This oil is œnanthic ether mixed with a variable proportion of acid. To obtain the pure ether this crude oil is again distilled, and the first quarter coming over is separated. This is agitated and heated with a

solution of sodic carbonate to remove the free acid. The separated ether is dried over lumps of calcic chloride, by which the last traces of moisture and alcohol are removed. The ether is a colourless oily liquid, with an overpowering vinous smell, and a sharp disagreeable taste. It has spec. gr. = 0·862, vapour density = 10·508, and boils between 225° and 230° C. It is very soluble in ether, alcohol, or even very dilute spirit, but almost insoluble in water. The fixed caustic alkalies readily decompose it into alcohol and œnanthic acid already described above. To the presence of this œnanthic ether is due the characteristic vinous smell which distinguishes all kinds of wine from every other fermented liquid. The flavour or bouquet, however, by which the wines of different vineyards and vines are distinguishable from each other, is produced by substances of a different nature.

Tartaric Ether, $C_4H_5(C_2H_5)O_6$, is also met with in wine. It behaves like an acid.

By the influence upon each other of the alcohols and acids present in wine a considerable number of compound ethers may be produced. For supposing five alcohols and five acids to be present they might produce twenty-five compound ethers, some or all of which might contribute their share to the flavour, such flavour altering as one or the other ether predominated. All these ethers occur in wine in extremely minute quantity only, and almost entirely elude ordinary analysis. However, in the manufacture of brandy enormous quantities of wine are distilled, and a considerable amount of so-called *fousel-oil* obtained, in which a number of the above-named volatile acids and ethers, as well as several different alcohols, have been detected.

Estimation of the Quantity of Ether in Wine.—The process is based upon the fact that there are two classes of compound ethers present in wine—one class being volatile, and having for its type acetic ether; the other being fixed, and having tartaric ether as its type. If a wine is carefully distilled the volatile ether will pass over into the distillate, while the fixed ether will remain with the matter in the retort.

The ether in the distillate may be estimated as follows:—The distillate is put into a flask and a quantity of decinormal soda solution added. The flask is stopped by a caoutchouc stopper, and then heated for some time, not exceeding six hours. The amount of alkali which has been neutralized is then ascertained.

The ether in the residue is decomposed by boiling with an alkali; the alcohol set at liberty is distilled over and estimated.

Thus, the amount of volatile ether is calculated from the equivalent of acid which it yields by decomposition, while the amount of fixed ether is calculated from the equivalent of alcohol which it yields by decomposition. Such small amounts of alcohol are best estimated as acetic acid, into which they are transformed by oxidation with bichromate and sulphuric acid.

Theory of the Limitation of Ethers in Wine.—According to Berthelot the amount of ethers found in any mixture of alcohols and acids is, after a certain time, a constant quantity, independent of the nature of the alcohols and acids present, but a function only of their relative amount. He gives the following formula for calculating the amount of alcohol contained in the compound ether of 1 litre of a mixture of acids, alcohols, and water, such as wine essentially is when etherification is complete. Let A be the percentage by weight of alcohol in the mixture; a be the amount of alcohol equivalent to the total free acid contained in 1 litre wine, on the assumption of its being acetic acid (46 alcohol equivalent to 60 acetic acid); y the proportion per cent. of a present as compound ether in 1 litre wine, when the alcoholic strength of the wine is A; and lastly, x be the amount of alcohol present in the compound ether of 1 litre of wine. Then—

$$y = 1{\cdot}17\,A + 2{\cdot}8$$
$$x = \frac{y \times a}{100}$$

In general, the results of analysis bear out the results of calculations according to this formula. Wines, however, which have not reached the state of equilibrium, *e.g.*, young wines, or wines which have been recently mixed with spirit, do of course not answer to it on analysis. We may thus, by the estimation of the ethers, judge of the age and genuineness of wines. Wines less than four years old will contain less ether than required by the formula; after four, and at six years, they will reach the maximum of etherification. If the wine be mixed with spirit, etherification will begin afresh, and again reach a maximum after a number of years. On the other hand, a wine prepared artificially, with addition of ether, will probably at once show a maximum, if not excess of ethers, and will then, instead of increasing in richness, remain stationary, or show a diminution of the ether with increasing age.

The proportion between the volatile and fixed ethers present in wines bears no relation to the amounts of volatile and fixed acids present. All the fixed acids are present already in the grape-juice, and their etherification can therefore begin as soon as alcohol begins to be formed during fermentation, and continue simultaneously with its production. Moreover, the amount of fixed acids is greatest at the beginning of the fermentation, decreasing as the amount of alcohol increases, on account of the lesser solubility of acid tartrate of potassium in alcoholic liquids. It may therefore be concluded that the amount of fixed ethers formed in a given time is greatest in quite young, or even still fermenting wine.

The volatile acids, on the other hand, are all formed during or after fermentation. If, therefore, fermentation has taken place under circumstances unfavourable to the production of volatile acids, little or no volatile acid will be present at first, but the amount will increase gradually with the age of the wine, or suddenly with the occurrence of such accidents as viscosity. In such a wine, therefore, the production of fixed ethers begins before that of

the volatile ethers. But the continually increasing amount of volatile acids, aided by their greater tendency to etherification, and the gradual decrease in the amount of fixed acid, soon reverses the condition, and causes the volatile ethers to preponderate.

Smell, Bouquet, Aroma, &c., of Wine.—The odoriferous substances which are more or less common to all wines, viz., the compound ethers, have already been considered above; but those which are characteristic of particular kinds of wine are as yet little studied chemically, no doubt because for their isolation very large quantities of material would be required. They may be divided into two classes: viz., such as are already present in the grape and are unaltered during fermentation, such as the flavour of the muscatel grape; and secondly, such as are formed during and after fermentation, partly out of substances already present in the grape, partly from matters formed during or after fermentation. The first class are found in what are termed aromatic wines, the second in bouqueted wines. The substances characterizing aromatic wines belong probably to the essential oils. The substances yielding the bouquet are not known at all; they can be obtained as tinctures; some of them can be produced from other natural products, particularly flowers. Thus the flowers of elder give a tincture which, when cautiously added to wine, produces the flavour of muscatel. This tincture is the common ingredient of Moselle wines; the tincture of the flowers of the vine itself produces a kind of Rhine-wine bouquet.

BERTHELOT endeavoured to extract some of the odorant substances by ether, from several litres of wine previously neutralized. The isolated ether, after evaporation at a low temperature, leaves a residue, being less than a thousandth part of the wine, possessing the characteristic bouquet and flavour of the wine. It is very liable to change, losing its odour at 40° C., or by exposure to air.

SUGAR.—The sugar contained in grapes is probably a mixture in molecular proportion of two different kinds of sugar, viz., fruit sugar and grape sugar—in fact, the same mixture as that produced by the action of acids on cane sugar, termed invert sugar. Cane sugar is never found in grapes; it is, however, sometimes added to must or to wine in large quantities—for example, to Champagne. In either case it is very soon changed into invert sugar, so that after the lapse of a few weeks only, cane sugar is no longer found in the wine to which it had been added.

During the fermentation of the must the fruit and grape sugar are decomposed, chiefly into alcohol and carbonic acid. Both sugars are not, however, decomposed in equal quantities, so that at the end of the fermentation generally more fruit than grape sugar is left. The sugar which remains permanently in the wine consists mainly of fruit sugar, with only a small admixture of grape sugar. In a few varieties of wine the permanent sugar consists entirely or partly of inosite. The proportion between grape and fruit sugar in wine varies with the kind of wine, and the condition of fermentation under which it has been produced. Although most frequently the fruit sugar remains in excess, sometimes the grape sugar is left in greatest quantity; and under certain rare conditions grape sugar only remains behind, while all fruit sugar is decomposed. The sugar, whether fruit or grape sugar, thus left undecomposed at the end of fermentation in pure natural wines, rarely amounts to more than 0·5 per cent., being generally much less. Even this small quantity is found in young wines only, and disappears as the wine becomes aged. In fortified wines, to which alcohol is added to prevent secondary fermentation, and concentrated must or the must from passulated grapes preserved with alcohol (Spanish "dulce," Portuguese "jeropiga"), or which are themselves made from raisins, whether like Tokay with must only, and without alcohol, or like Tintilla de Rota, with boiled must but without alcohol (*arrope*), or like the liqueur wines with alcohol only, the sugar ranges from 2 or 3 per cent. to upwards of 20 per cent.

As the various kinds of sugar and their chemical properties are described at full length in other parts of this work, it is not necessary to enter upon them in this article. We shall therefore consider only the special preparation to which it is necessary to subject wines for detecting or estimating quantitatively the sugar which may be contained in them.

Chemically, the sugar is best *detected and estimated* by FEHLING'S method. Before this can be applied the wine must be subjected to some treatment which shall remove not only colour, but also some substances which, though not being sugar, yet also reduce an alkaline copper solution. Light white wines are for that purpose shaken with animal charcoal. Dark coloured wines, however, and wines containing more than 2 per cent. of solid matter, must be diluted. Wines with between 2 and 4 per cent. of solid matter should be diluted with from two to five times their bulk of water; while wines containing upwards of 4 per cent. are diluted so as to yield a mixture containing about a half per cent. of residue (ascertained by TABARIE'S method). The wines are decolorized and purified by lead acetate solution, made by dissolving 1 part of sugar of lead in 10 parts of distilled water. Thus, to 100 c.c. of light white wines, 20 c.c. of the lead solution are added, and the mixture, after being well stirred, is allowed to stand a short time and is then filtered. The clear filtrate is next shaken up with some animal charcoal, and again filtered; this second filtrate will be found generally perfectly colourless. Of wine of the second category 50 c.c. are mixed with 10 c.c. of lead acetate solution, and this mixture is then diluted with water so as to form from 100 c.c. to 300 c.c. of solution; this is then filtered, shaken with animal charcoal, and again filtered. Of the third class of wines only 30 c.c. need be taken, 5 c.c. of lead acetate added, and then water, so as to yield a mixture giving about 50 c.c. of solution for each per cent. of residue in the original wine. Filtration and charcoal treatment follow as before. In practice

it is convenient to measure the wine with a pipette, and pour it into a glass-stoppered flask of the required capacity, marked on the neck. The acetate of lead is added to the wine, and the flask is filled up to the mark with distilled water. The clear filtrate thus obtained is now fit for charcoal treatment or for testing. It is sometimes recommended to render the wine alkaline with lime water before adding the acetate; but this should be avoided, inasmuch as in alkaline solutions grape sugar is precipitated to some extent by plumbic acetate, and therefore lost to the subsequent copper test. To the decolorized solution the alkaline copper solution is applied in the usual manner.

The Optical Examination of Wine for Sugar is conducted as follows:—To 100 c.c. of wine 20 c.c. of the solution of plumbic acetate are added; the mixture is well shaken, and after standing a short time, filtered. The filtrate is shaken with a little animal charcoal, and again filtered. The colourless and bright liquid is filled into the tube of the saccharometer, and the rotation determined. Nearly all wines turn the plane of polarized light to the left. The same filtrate, after suitable dilution as before described, is used for the chemical test.

Wine contains a mixture of fruit and grape sugar (not being invert sugar), and the amount of circular polarization shown by such a mixture depends upon the proportion in which these sugars stand to each other. As one part of grape sugar turns about as much to the right as half a part of fruit sugar turns to the left, a mixture of these two in this proportion would thus show no polarization at all; the mixture would turn to the left if more fruit sugar were present, to the right in presence of more grape sugar. But whatever be the proportion between them, one-half part of fruit sugar will always neutralize the optical effect of one part of grape sugar, and only the excess of either will have a free optical effect. If the proportion between the fruit and grape sugar present in wine were always the same, it would be possible to fix a relation between the amount of circular polarization shown and the quantity of sugar present, and a single optical observation would enable us to estimate that quantity. If, on the other hand, the proportion between fruit and grape sugar were variable, the optical test alone would be valueless as an indicator of quantity. Chemically, however, these two varieties of sugar act alike, and whatever therefore be the proportion in which the two are present, the sum of their quantity can be estimated chemically; and this, coupled with the optical test, enables us to calculate the proportion of fruit and grape sugar present in any mixture. In pure natural wines from the Rhine and the Gironde there is about 1 per cent. of sugar found chemically, which, by the combination of the optical with the chemical, is shown to consist of about 3 parts of fruit sugar and 1 part of grape sugar. Fine Madeira, fifty years in bottle, showed very nearly the same quantities. High class Port wines also exhibit these proportions.

In low class wines the fruit sugar diminishes relatively to the grape sugar. Thus, cheap Port contained 1·971 per cent. sugar, and in this 1 part of grape—upon 1·35 parts of fruit sugar. Marsala contained 4·329 per cent. of sugar, and in this upon 1 part of grape—0·84 part of fruit sugar. Cheap sherry contained 4·617 per cent. of sugar, and in this upon 1 part of grape—0·81 part of fruit sugar. Elbe sherry (being Greek wine, mixed at Hamburg with must syrup and corn brandy) contained 6·512 per cent. of sugar, in which 1 part of grape sugar was accompanied by 0·73 of fruit sugar.

Exceptions to this rule are met with in very old high class wine, in which also the fruit sugar sinks below the proportion observed in natural wines, but never so low as in the case just quoted. Thus, a fifty year old high class sherry contained 2·110 per cent. sugar, and in this upon 1 part of grape—1·26 parts of fruit sugar.

If the proportion of fruit sugar sink to about half that of grape sugar the wine shows no polarization at all, for the left-handed polarization of the fruit sugar is then just neutralized by the right-handed one of the grape sugar. This condition was found to exist in a sample of natural Port, in which chemical tests showed the presence of 0·177 per cent. sugar, while not a trace of polarization was perceptible when examined in Jellett's saccharometer. When the proportion of the fruit sugar sinks still lower, the wine begins to turn to the right; in such a case it is frequently assumed that grape sugar had been added to the wine. But this is not necessarily the case, as under certain rare conditions of natural fermentation fruit sugar chiefly is destroyed, grape sugar, on the contrary, preserved; so that the prevalence of grape sugar in wine must not necessarily be taken as indicating adulteration with artificial sugar, although it indicates in most cases that must syrup has been added to the wine.

The sugar contained in Champagne is chiefly invert sugar, formed by the action of the acids in the wine on the cane sugar added in the liqueur.

Glycerine, $C_3H_8O_3$, is always present in wine in the proportion of about one-fourteenth part of the alcohol, and therefore exercises a considerable influence upon the taste. It is formed from sugar during fermentation, 100 parts of cane sugar or 105·26 parts of grape sugar yielding 3·64 parts of glycerine. It may be extracted from wine by the following process of Pasteur:—Half a litre of wine is shaken with 40 grams. of animal charcoal, and after standing for twenty-four hours, filtered. The charcoal is well washed with cold water, and filtrate and washings are evaporated on a water bath to 200 c.c. At this point they are neutralized with hydrate of lime, and then evaporated to dryness. The residue is treated, in the evaporating dish, with a mixture of 2 parts of ether and 1 part of alcohol. The ethereal solution is evaporated on a water bath, and finally dried *in vacuo* over oil of vitriol; the residue, consisting mainly of glycerine, is then weighed. It contains, however, variable quantities of fruit sugar, and other extractive matters.

Colouring Matters.—Many varieties of young

wines are almost colourless, such as Champagne and Moselle; others, particularly older ones, are purely yellow, such as Sauternes. Older white wines, so-called, present all varieties of shade of yellowish, up to dark-brown. These colorations are produced by the oxidising effect of the air upon the so-called extractives and the tannic acid, which latter is extracted by the juice or wine from the husks, kernels, and stalks. The wine during fermentation and repose in the cask also extracts tannin from the oak. During ripening all white wines, so-called, become of a darker colour, and in many cases shed a brown deposit, the fully oxidised extractive matter and tannin, which are incapable of remaining in solution. Colour is, therefore, a necessary result of age in nearly all white wines; and therefore colour is frequently imparted to young wines, for the purpose of giving them the appearance of age, by caramel or burnt sugar, and by must boiled down to a brown syrup. Sometimes the entire must is boiled down to a syrup (*arrope*), as in the case of the Tintilla de Rota; sometimes only a portion of the must is concentrated and added to the crude must, to increase its specific gravity, its colour, and its temperature, as is not rarely done in the white-wine districts of Portugal. The tints of all kinds of *red wine*, whether they are slightly rose-coloured or almost black and impenetrable to light, are produced by peculiar colouring matters deposited originally either in the pulp or in the husk of the grapes. An example of the *soluble colouring matters* contained in solution in the pulp of grapes is yielded by a variety of vine, called the "teinturier" or dyer, which is extensively grown in France and Spain for the production of black wines fit for colouring others. This soluble colouring matter is similar to that contained in elderberries or black currants. The colouring matters, which give their tints to the wines of Burgundy, the Médoc, and a few other districts of France, and to the wines of the Alto Douro are, in the grape, deposited in the husk, and are not soluble in the unfermented juice; they are extracted by the made wine only, and all red wine has for this reason to be fermented with the husks.

The colouring matter of red wine can be precipitated by lead acetate; the washed precipitate is decomposed by hydrothion and extracted with alcohol and some acetic acid. The pale red solution on evaporation becomes red at first, then violet, and next blue; when dry the pigment is bluish black, like black lead; it is insoluble in alcohol, water, ether, chloroform, carbon disulphide, and oil of turpentine, but soluble in alcohol acidified with acetic or tartaric acid. Alkalies colour it *green*, and by short contact change it so that the restoration of the acid reaction of the solvent fails to restore the red or violet colour. The elementary composition of the colouring matters from juice has not yet been ascertained. That from husks of the gamay (Mâcon) vine was found by Glénard to have the composition represented by the formula $C_{20}H_{20}O_{10}$; the red colouring matter of the carignane and grenache (Roussillon) vines was found by Gautier to be $C_{21}H_{20}O_{10}$ and $C_{23}H_{22}O_{10}$ respectively. Roussillon wine also contains a blue colouring matter, represented by the formula $C_{63}H_{60}FeN_2O_{30}$, being three times the formula $C_{21}H_{20}O_{10} + FeN_2$; this is said to be a ferrous salt of a nitrogenized red colouring matter. From this it appears that red wines owe a part of their tonic qualities to a ferruginous ingredient.

The colour of wine is determined by the amount of the blue-colouring matter present, and the quantity of free acid which acts upon it. The more free acid is present the more red will the wine appear, and with the decrease of the acidity the colour will approach towards the violet.

The crust which Port wine forms in bottles contains oxidised tannin in an insoluble state, colouring matter in an insoluble state, and potassic tartrate. The changed tannin and colouring matter are probably in combination with each other.

Wines are sometimes coloured artificially by the colouring matters of other kinds of fruit. The most commonly used are elderberries; next in favour are black cherries; bilberries are used more rarely. But the staple red wines of trade, such as Medocs, Alto Douros, Spanish reds, contain naturally enough or more than enough of colouring matter, and what is frequently said about their adulteration with some kinds of abominations, such as logwood, cochineal, fuchsine, &c., is either mere romance, or founded upon occurrences of such rarity as to be undeserving of further consideration.

Ammonia.—Small quantities of ammonia are either present in the grape-juice, or are formed during fermentation out of the albuminous substances. The greater part of this ammonia is precipitated during the progress of fermentation as ammonio-phosphate of magnesia. In some wines the ammonia is accompanied by minute traces of trimethylamine.

Albumen.—Grape juice contains a large amount of albuminous matters, which are partly deposited spontaneously, as fibrine is from blood, or remain in solution and are partly absorbed by the fungi which develop in the course of fermentation. The albumen which remains in solution in the fermented wine renders the wine liable to secondary fermentations and so-called diseases, as long as it contains any considerable number of the germs which produce these conditions during their further development. The effect of albumen in the wine is counteracted by the presence of tannin; red wines may therefore be fined with white of egg without damage, while white natural wines require isinglass for fining; strong brandied wines may also be fined with white of egg, *e.g.*, sherries. Natural wines containing excess of albumen may be corrected by being heated, according to Pasteur, or by receiving a certain amount of tannin; tincture of catechu is frequently used for this purpose, particularly in the case of Champagne.

Albumen is detected in wine by the addition of strong chlorine water; a precipitate thereby produced is albumen, probably in a chlorinated state. Older wines give no longer a precipitate with chlorine

water; in this case ferrocyanide of potassium and acetic acid may yet produce one. If neither heat nor these reagents produce deposits, the wine may be considered to be almost free from albumen.

Tannin.—The juice of grapes is perfectly free from tannin; but skins, seeds, and stalks contain considerable quantities of this astringent principle, and yield it to the wine which is fermented with them. The tannin of wine is not identical with any of the known tannins of other plants, but peculiar, and on being boiled with dilute sulphuric acid yields sugar and an acid which is not gallic acid. The tannin of white wine is sometimes derived from the oaken casks in which the wine is kept. Its presence may be detected by the inky coloration produced by the addition of ferric chloride and potassic acetate; it may also be precipitated by a solution of gelatine. Tannin reduces copper salts in alkaline solution.

Extractives.—These consist of nitrogenous matters, being acids and alkaloids; they contribute greatly to the body and fulness of taste of the wine. Their exact nature and composition have not yet been determined.

Ash.—When wine is evaporated and the residue burnt, the mineral constituents remain behind in the form of ash. This consists chiefly of potassic carbonate, chloride, sulphate and phosphate, sodic chloride, calcic phosphate and carbonate, with traces of magnesia, iron, silica, and sometimes of alumina and manganese. Potassic and calcic carbonates are not, as such, contained in the wine, but are produced by the combustion of the tartrate or malate of potassium and calcium. From the ash of pure natural wines carbonates and chlorides are scarcely ever absent. Sometimes, however, if the wine has been subjected to much sulphuring, it may contain an excess of sulphuric acid, which, during the evaporation and incineration, drives out all the volatile acids; the ash in such a case consists exclusively of sulphates and phosphates. The ash of wine made from must to which plaster of Paris had been added, or which had itself been digested with plaster of Paris, scarcely ever contains carbonates, and is very frequently free from chlorides, on account of its containing an excess of sulphuric acid formed by double decomposition from the calcic sulphate and potassic bitartrate.

Estimation of Ash.—The method is the same as that used for the estimation of ash in organic substances generally. Great heat must be avoided, in order to prevent fusion of the salts and inclosure of carbon. The amount and nature of the ash left by a wine is a very valuable means for judging of its genuineness, as is partly evident from the foregoing paragraph; and its examination should therefore never be neglected.

Analysis of Ash.—This is performed by the ordinary methods in use. When chlorides are not found in the ash, and in all cases in which the ash contains excess of sulphate, the chlorine has to be determined in the wine, and the difference in the amounts noted. It is perhaps preferable to do this in all cases whatsoever, as the tartaric and malic acid of wine expel some hydrochloric acid already during evaporation, so that the amount of chlorine found in the ash is never the entire quantity which was present in the wine itself. In the majority of cases the sulphuric acid found in the ash is the total quantity present in the wine; this is always the case if the ash contains either carbonates or chlorides. Sometimes, however, there is more sulphuric acid in the wine than can be neutralized by the bases present, and in such a case part of it is lost during ignition; the ash in such instances is free from carbonates and chlorides. This is sometimes the case with wines which have been impregnated with sulphurous acid only; more frequently, however, this excess of sulphuric acid comes into the wine through the practice of adding plaster of Paris to the must, as is done with all sherries, and superadding sulphurous acid thereto, as is done with the commoner sorts of sherries. In these cases it is necessary to estimate the sulphuric acid in the wine itself.

The amount of ash varies considerably in different classes of wines; in pure natural wines it amounts generally to from 0·15 to 0·30 per cent.; in wines which have been plastered the ash rises to 0·5 per cent. and upwards; and in all those in which the excessive acidity has been neutralized by an alkali or by chalk, the ash may rise considerably above this amount.

Total Solid Constituents.—The solid constituents may be estimated by evaporating a little wine to dryness, &c. The residue should be dried at 110° to 115°, until it ceases to lose weight when kept for two or three hours at that temperature. During this process the residue always suffers some change, and does not, therefore, represent the whole of the constituents. The solids in wine are therefore preferably estimated as a part of Tabarie's method of estimating alcohol, already described. In thus estimating the total solid constituents of a wine by the specific gravity of the dealcoholized wine, it is necessary to subtract from the percentage of extract thus estimated the percentage of ash found in the same wine; or if the amount of extract without the ash is required, twice the percentage of ash has to be subtracted from the percentage found, according to the specific gravity. In wines containing but little ash, this correction (based upon the greater density of the solution of the mineral constituents, which is about double that of sugar and extractives) is not very important; but in wines in which the ash is from 0·3 to 0·5 a serious error would be committed by omitting the correction.

Programme of an Analysis of Wine.—All the apparatus and chemical reagents known to be required being ready and in good order—

1. Heat the water-baths to boiling, put on two platinum and two porcelain crucibles, one evaporating dish of 400 c.c. and one of 150 c.c. capacity.

2. Take two bottles of the wine to be analyzed, mix in a large bottle, shake to expel carbonic acid, take temperature, bring temperature to 15°·5, or to that of the workroom; for it is not advisable to work with the wine at a temperature below that of the room.

3. Measure with pipette 20 c.c. wine into each of the following vessels: — Two porcelain and two platinum crucibles; three beakers (Nos. 1, 2, and 3), and two wide-mouthed stoppered bottles (*a* and *b*). These quantities are to serve for the estimation of the fixed acid, total residue, ash (two), total acid, chlorine, sulphuric acid, bitartrate of potassium, total tartaric acid.

4. Measure with flasks 100 c.c. and 250 c.c. into the fore-mentioned evaporating dishes on water-bath (de-alcoholized wine and fixed ether).

5. Measure 250 c.c. wine into still, add tannin and potash, heat and collect distillate (alcoholic strength).

6. While distillation, &c., is going on take specific gravity of wine, estimate total acidity (beaker No. 1), take beaker No. 2 and No. 3, precipitate chlorine and sulphuric acid, set aside; precipitate tartar and total tartaric acid in bottles (*a* and *b*), set aside.

7. When distillation is finished, make up distillate to 250 c.c., at original temperature of wine; clean out still, and set 250 c.c. fresh wine distilling, without any addition (volatile ethers); take specific gravity of first distillate.

8. When the contents of the four crucibles have been heated sufficiently long on water-bath, place one of the porcelain crucibles into air-bath, heated to 110°, till weight remains constant (total dry residue); estimate acidity of the residue in another of the porcelain crucibles (fixed acids); heat the two platinum crucibles to dull red heat over Argand burner or in muffle, till ash is white; weigh ash in one crucible, and use it for estimating alkalinity for determining the portion insoluble in water, and the phosphoric acid in this insoluble portion; the ash in the other crucible, which need not for this purpose be burnt perfectly, use for estimating total phosphoric acid.

9. When the 100 c.c. in small dish have evaporated to about 40 c.c., transfer to 100 c.c. flask, cool and fill up to 100 c.c. with distilled water at original temperature; take specific gravity of this de-alcoholized wine (used for calculating total residue and alcoholic strength).

10. When 250 c.c. in large dish are evaporated to about 40 c.c. transfer to small still, render alkaline, &c. (fixed ethers).

11. Take 100 c.c. wine, add 10 to 20 c.c. acetate of lead solution according to colour, shake and filter through dry filter, shake up with animal charcoal, filter; estimate amount of circular polarization in this filtrate (with very sweet wines less than 100 c.c. may be taken).

12. Dilute filtrate (11) to the necessary extent, and estimate sugar in filtrate by copper test.

13. After twenty-four hours' standing collect precipitates of chloride of silver and sulphate of barium from beakers 2 and 3; wash, dry, ignite, and weigh (total chlorine and sulphuric acid).

14. After forty-eight hours' standing collect precipitates in bottles (*a* and *b*), wash with ether alcohol, and estimate acidity with decinormal soda (bitartrate of potassium and total tartaric acid).

ZINC—*Spelter. Zink*, German. Atomic weight, 65·2: Symbol, Zn. Zinc ores were known from a very early date by the Greeks and Romans, who used them to produce brass and bronze. It was first mentioned as a metal by PARACELSUS about 1530, and was noticed as a waste product in the smelting of copper in the 17th century. LŒHNEYSS says (1617):—"When the people are employed in melting, there is found under the furnace, in the crevices of the walls, a metal which is called *zinc* or *counterfeht*. This metal has a great resemblance to tin, but it is harder, and less malleable. It is not much valued, and the work-people collect it only when they are promised drink-money." BECKMANN KENKELL is accounted to have been the first who procured zinc directly from calamine (zinc carbonate), in 1741. VON SWAB obtained it by distillation of calamine in 1742. In 1743 a zinc factory was established at Bristol (WATSON, *Chem. Essays*). At this time most of the zinc used in Europe was imported from India and China; but the manufacture in Europe, principally at Silesia, continued to grow till, in 1820, the exports to India from England almost balanced the total imports. Zinc is also manufactured in Belgium, Poland, and Missouri, U.S.

The metal is extensively used in brass-founding, for coating or *galvanizing* iron, for making zinc-white, and various other purposes.

The most important ores of zinc are *Red oxide* or *Spartalite* (ZnO, contaminated with manganese oxides), *Zinc blende* (zinc sulphide, ZnS), *Calamine* (zinc carbonate, $ZnCO_3$), and *Silicious calamine* or *Zinc-glance* (zinc silicate, Zn_2SiO_4,H_2O), and *Smithsonite* (anhydrous silicate Zn_2SiO_4).

Zinc is of a bluish-white colour. When polished it has a high metallic lustre; it is brittle, and has a crystalline fracture at ordinary temperatures; but when heated to between 100°–150 C., it becomes malleable, and can be drawn into wire or rolled into sheets. At 210° C. it again becomes brittle, and can then be crushed to powder. When rubbed, zinc emits a peculiar odour. The specific gravity of cast zinc is 6·862, but is increased by forging to 7·21. It melts at 412° C., and boils at 1040° C. (DEVILLE and TROOST). Zinc volatilizes at a red heat, the vapour taking fire and burning in the air with an intensely luminous bluish-white flame, producing zinc oxide, which condenses in voluminous flocculent masses. At a red heat zinc decomposes water; the same action is produced at ordinary temperatures, under the influence of dilute acids, and if the zinc be impure, with considerable energy. Pure zinc dissolves very slowly in acids; but if touched by any less positive metal or body than itself a galvanic couple is formed, and its solution is rapidly effected. In water or moist air zinc is quickly covered with a grey film of oxide, which, from its insolubility, protects the metal from any further attack. Hence the advantage of coating iron with zinc. Zinc is unoxidised by dry air. In caustic alkalies it dissolves with evolution of hydrogen, forming zincates of the metals, thus:—

$$Zn + 2KHO = K_2ZnO_2 + 2H.$$

Zinc is a diatomic metal. The alloys which it forms with other metals have nearly all a tendency to be hard and brittle. (See COPPER ALLOYS).

METALLURGY.—Tin ores, employed at Bristol and Birmingham, are obtained from the Mendip Hills and from Flintshire; those at Sheffield from Alston Moor, Cumberland, and from Derbyshire. Blende is also obtained from Cornwall, and is distilled after roasting to drive off the sulphur. The ore is broken up into fragments about the size of a pigeon's egg, and roasted at a red heat in reverberatory furnaces, after which it is mixed with its own bulk of coal and ground under a pair of edge rollers; or, the blende having been roasted likewise, a charge is compounded of 1 part blende, 1 part calamine, and 2 parts anthracite The mixture is placed in crucibles 4 feet high, inclosed in a conical brickwork chimney, similar to that of a glass furnace or pottery kiln. A number of openings are constructed in the cupola, corresponding to the pots in the furnace, in order

Fig. 1.

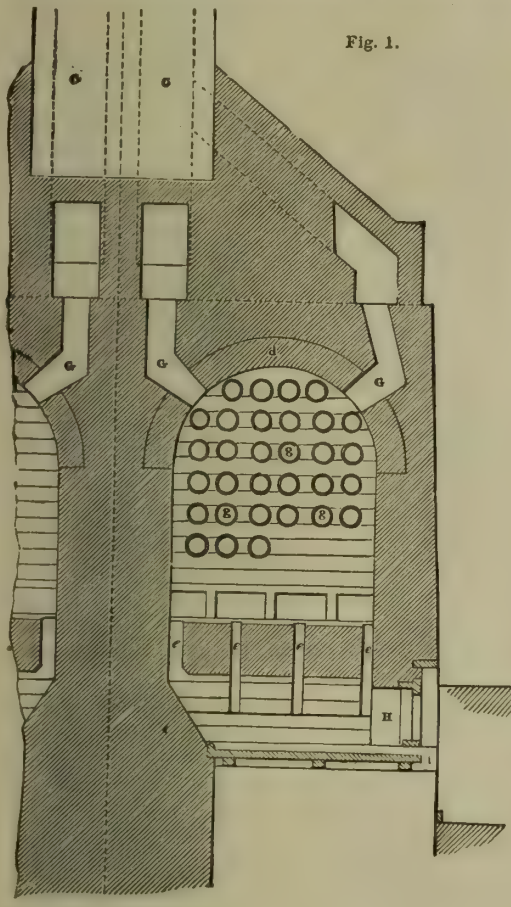
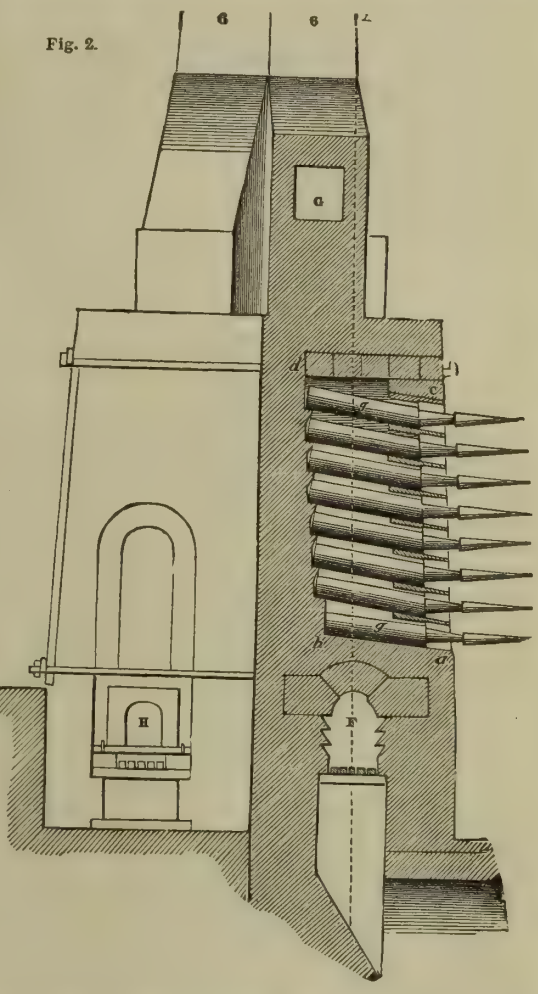


Fig. 2.



to charge the crucibles. Each crucible has a central iron pipe, proceeding from near the top through the bottom, to a water cistern 6 or 7 feet below the hearth of the furnace. To charge the crucibles they are heated to redness in a reverberatory furnace, and are then placed in the smelting chamber and the mixure of ore and coal introduced; the outlet at the bottom of the crucible being closed by a plug of wood. The fire is then urged till the zinc vapour ignites, upon which well-luted covers are placed on the several pots; the pipes are inserted in their bottoms, and the distillation allowed to proceed; the temperature being brought to a high white heat. The metal is condensed in the iron pipes and runs into the cistern below. This process is to a great extent replaced by the Belgian and Silesian methods.

Belgian Process.—The selected ore is calcined either in a reverberatory furnace or in a conical kiln. The roasted ore is then ground, mixed with charcoal or fine coal in the proportion of 1680 lbs. of roasted ore (calamine or blende) and 840 lbs. of coal dust, this being the charge for a furnace. The mixture is slightly damped and introduced into cylindrical fire-clay retorts, closed at the ends which are inserted into the furnace and open at the other (*g*, *g*, Figs. 1 and 2) by means of a semi-cylindrical scoop. To each open end is fitted a conical pipe of sheet iron, and this in

turn has appended to it a beak of the same material but much smaller. The retorts are placed in the furnace shown in section in Figs. 1 and 2, the latter in the line A B of the former. The stack consists of four distinct furnaces, each in the form of a semi-cylindrical chamber, 8 feet 8 inches from the highest point of the arched roof to the floor, the back of the chamber being constructed so as to recede slightly from the bottom or floor upwards, as shown by *b d*, in Fig. 2, and the front, *a c*, being left open for the convenience of introducing the retorts. The fire is shown at F, the combustible gases and other products passing upwards through four apertures in the grate, shown at *e e e*, and thence by a double flue, G G, finding an exit overhead into the chimney, C. The latter forms one massive construction, embracing the four outlets, each closed by a damper. In each of the chamber furnaces forty-two retorts, *g g*, are heated; these being placed in rows one above the other, as shown in the drawing, the posterior end resting upon a ledge made for the purpose in the masonry or brickwork. In the front the distilling cylinders are supported by plates of cast-iron, so fixed at each side of the face of the furnace as to allow the cylinders to slope downwards from the back to the front.

The furnace is brought to a bright red heat, and the retorts which have been heated in a reverberatory furnace are then fixed in their places. The charge is filled in by slow degrees for a period of three or four days, or until the furnace is found to be in working condition. When the zinc vapour is evolved and inflames at the mouths of the retorts, the condensing tubes are fitted on and the distillation commences. From time to time the beaks of the retorts are removed, and the fluid zinc is raked into ladles and cast into ingots. The oxide is returned to the furnace with the next charge.

The bottom range of retorts is seldom filled in this country on account of their liability to be broken.

Silesian Process.—The ore and powdered coal are distilled in muffles made of fire-clay and broken muffles—baked and annealed after the fashion of glass pots. These are set in rows in a furnace provided with suitable openings. The front of the muffle has two apertures. The lower one serves to remove the residues after each distillation; the upper has a hollow clay arm fitted to it, bent at right angles, and open at the bottom as well as at the top, and also a small door at the top of the bend through which the muffle can be charged. From six to ten muffles are set in a row. The fuel in the older works is coal, but all the new works are provided with SIEMENS' gas furnace.

Galvanizing.—The process of coating iron with zinc, known under the inappropriate title of "galvanizing," was discovered by MELOUIN in 1742. Of late years iron coated with zinc has come largely into use as a roofing material, for making spouts, gutters, buckets, and in fact for all the purposes for which sheet iron can be used. MELOUIN'S process is followed with a few modifications even at the present day. The iron is cleansed by immersion for a few minutes in an acid bath, composed of oil of vitriol and water, or of hydrochloric acid and water, or of equal volumes of the two acids and water; it is then scrubbed with sand, washed with water, and dipped in a concentrated solution of ammonium chloride, taken out, and subsequently introduced into a bath of melted zinc, covered with fat or rosin, to prevent oxidation, and stirred in it till the zinc alloys with its surface. Of late years a few lbs. of tin have been added to the zinc to improve the appearance of the plates.

H. W. CRAWFURD in 1837 patented a process of coating iron with zinc, the chief characteristic of which is covering the zinc bath with a thick layer of sal-ammoniac. Thick pieces of iron are heated before immersion, to avoid cooling the zinc. Nails, &c., are cleaned with hydrochloric acid, dried in a reverberatory furnace, and plunged in the zinc bath for one minute. When fished out with a skimmer they are generally soldered together, and are separated by heating to redness with charcoal, and then shaking till cold.

Wire is galvanized by reeling it through a zinc bath covered with a layer of ammonium chloride.

MALLET prepared his iron for galvanizing by dipping it in a saturated solution of zinc chloride and ammonium sulphate, after which he treated it with a hot amalgam consisting of 1 part of mercury with 6½ of zinc; 1 pound of sodium being added to each ton of the amalgam.

In MOREWOOD and RODGER'S process the iron is first tinned, and then immersed in a zinc bath covered with sal-ammoniac, to which some earth has been added to prevent its too rapid volatilization.

A large wooden bath is filled with a dilute solution of tin chloride, in the proportion of 2 quarts of saturated solution to 300 gallons of water. Over the bottom of the bath is strewn a thin layer of granulated zinc; upon this rests a cleaned iron plate, then another layer of zinc, and again a plate of iron, and so on till the bath is full. The zinc and iron form a voltaic couple, which in two hours precipitates the tin upon the iron in a dull uniform coat. The plates are transferred to the zinc bath while still wet, and are passed through it by means of iron rollers.

ZINC WHITE, ZINC OXIDE, ZINC, CARBONATE, and their hydrates—see PIGMENTS.

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