PART III

THE SYSTEMATIC STUDY OF THE ELEMENTS, BASED UPON THE PERIODIC CLASSIFICATION.

CHAPTER I

THE ELEMENTS OF GROUP VII. (FAMILY B.)

Fluorine, F	19.00	Bromine, Br	79.96
Chlorine, Cl	35.45	Iodine, I	126.97

THE first to be discovered, and the most important element of the group, is chlorine, which is a constituent of sea salt (sodium chloride). The term *halogen*, signifying sea salt producer, has been applied to this family of elements, on account of the close resemblance between their sodium salts and sea salt. This family exhibits, in a marked manner, many of the features which are found to exist in most chemical families of elements.

In their general behaviour they strongly resemble one another, and readily displace each other in combinations without producing any very marked change upon the character of the compounds. They each unite with hydrogen, giving rise respectively to hydrofluoric acid, HF; hydrochloric acid, HCl; hydrobromic acid, HBr; hydriodic acid, HI.*

These hydrogen compounds are all colourless gases, which fume strongly in the air; they are extremely soluble in water, and are strongly acid in character. In combination with potassium and with sodium, the halogens form a series of compounds, which are similarly constituted, and which closely resemble each other in their

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* Some chemists name these compounds hydrogen fluoride, hydrogen chloride, hydrogen bromide, hydrogen iodide respectively, and employ the names hydrofluoric acid, hydrochloric acid, &c., to denote the aqueous solutions only.

habits. Their similarity of composition is expressed in the following formulæ :—

Compounds with potassium, KF, KCl, KBr, KI.
Compounds with sodium, NaF, NaCl, NaBr, NaI.

The physical properties of the elements exhibit a regular gradation with increasing atomic weight ; thus, fluorine and chlorine are gases, bromine is liquid, while iodine is solid at ordinary temperatures. In their chemical activity they also show the same gradual change ; thus, in the case of their combination with hydrogen, when fluorine and hydrogen are brought together, combination instantly takes place with explosion, even in the dark. Chlorine and hydrogen do not combine in the dark, but in diffused daylight they unite slowly, and in direct sunlight their combination takes place suddenly with explosion.

Bromine vapour and hydrogen do not combine even in direct sunlight, but a mixture of the two gases ignites in contact with a flame, yielding hydrobromic acid, while iodine vapour and hydrogen require to be strongly heated in contact with spongy platinum to effect their combination. This difference in the activity of the halogens towards hydrogen is seen by a comparison of the heats of formation of their hydrogen compounds, thus—

$$\begin{aligned} H + F &= HF + 38{,}500 \text{ cal.} \\ H + Cl &= HCl + 22{,}000 \text{ ,,} \\ H + Br &= HBr + 8{,}440 \text{ ,, } * \\ H + I &= HI - 6{,}040 \text{ ,, } \dagger \end{aligned}$$

Although a strong resemblance exists between all the members of the halogen family, the element fluorine, which is the *typical* member (see page 115), stands marked off from the others in many of its attributes. Thus fluorine exhibits a great tendency to form double salts which have no counterpart among the compounds of the other elements of the family, and at temperatures below 32° the molecule of hydrofluoric acid consists of two atoms of hydrogen and two of fluorine, having the composition H_2F_2.

FLUORINE.

Symbol, F. Atomic weight=19.

History.—This element, the first of the halogen series, was the most recent to be isolated, it having baffled all attempts to

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* This value refers to bromine in the liquid state.

† Iodine as solid.

obtain it until the year 1886, when Moissan succeeded in solving the problem.

Occurrence.—Fluorine occurs in considerable quantities in combination with calcium in the mineral *fluor spar* (CaF_2), which is found in cubical crystals. On account of the occurrence of this mineral in large quantities in Derbyshire it is frequently termed *Derbyshire spar.* It is a constituent also of *cryolite*, Na_3AlF_6, *fluor-apatite*, $3P_2O_8Ca_3,CaF_2$, and many others. In small quantities fluorine is found in bones, in the enamel of teeth, and also in certain mineral waters.

Mode of Formation.—When an electric current is passed into an aqueous solution of hydrochloric acid, the acid is decomposed into its elements, chlorine being liberated at the positive electrode, while hydrogen is evolved at the negative. When aqueous hydrofluoric acid is treated in the same way, the water only is decomposed, oxygen and hydrogen being liberated. Davy found that the more nearly the acid approached the anhydrous condition, the less easily did it conduct electricity; and that in the perfectly pure state, that is, entirely free from water, hydrofluoric acid was a non-conductor. Moissan's recent success in the isolation of fluorine depends upon the discovery that a solution of the acid potassium fluoride, HF,KF, in anhydrous hydrofluoric acid is an electrolyte, and that by the passage of an electric current through this solution fluorine is disengaged at the anode, or positive electrode, and hydrogen is evolved at the cathode.

The primary products of the electrolysis are potassium (at the cathode) and fluorine at the anode. The potassium then reacts with the hydrofluoric acid, re-forming potassium fluoride and liberating an equivalent of hydrogen—

$$2KF = 2K + F_2.$$
$$2K + 2HF = 2KF + H_2.$$

Or, expressed in the form of ionic equations—

$$2K^{\cdot} + 2F' = 2K + F_2.$$
$$2K + 2HF = 2K^{\cdot} + 2F' + H_2.$$

The reaction is performed in a U-tube made of an alloy of platinum and iridium, a material which is less acted upon by the liberated fluorine than platinum alone. The apparatus has two side-tubes (Fig. 89), which can be either closed with a screw cap, C, or connected to platinum delivery tubes by means of the union D. The two limbs of the tube are closed by means of stoppers made of fluor spar, shown in section at S, and which can be securely screwed into the tube. These serve to insulate the electrodes, which are constructed of the same platinum-iridium alloy. The anhydrous hydrofluoric acid is introduced into the apparatus, and about 25 per cent. of its weight of the acid potassium fluoride is added, which really dissolves in the liquid. The tube is immersed in a bath of methyl chloride (M, Fig. 90), which boils at −23°; the supply being continuously replenished from the reservoir B, while the vapour is drawn away by the pipe C. On passing a current from 20 to 25 Grove's cells through the apparatus, fluorine is evolved at the positive electrode, and hydrogen is liberated at the negative.*

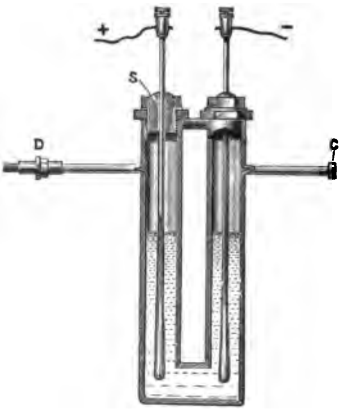

FIG. 89.

Properties.—Fluorine is, of all known elements, the most chemically active. It is on account of its intense chemical affinities that it so long resisted all attempts to isolate it, as when liberated from combination it instantly combined with the materials of the vessels in which the reactions were made. It is impossible to collect this gas by any of the usual methods, for it decomposes water and instantly combines with mercury. It also attacks glass, so that it can only be collected by displacement of air in vessels of platinum. Fluorine is a pale yellowish-coloured gas, appearing almost colourless when viewed in small quantities. The smell of the gas is very characteristic—it is irritating to the mucous membranes, and is not unlike the odour of the mixture of chlorine and chlorine peroxide, evolved from potassium chlorate and hydro-

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* More recently Moissan employs a copper tube of 300 c.c. capacity, fitted with large platinum electrodes. By keeping the temperature about −50°, and using a current of 15 ampères, he obtains the gas in large quantities.

chloric acid. Whether the smell actually perceived is the true smell of fluorine is doubtful, for when fluorine comes into contact with the moisture in the nostrils water is decomposed, with the formation of ozonised oxygen and hydrofluoric acid.

Fluorine not only decomposes potassium iodide, with liberation of iodine, but also displaces chlorine from sodium chloride.

It combines directly with a large number of elements with intense energy; in contact with hydrogen it instantly explodes. Iodine, sulphur, and phosphorus first melt, and then take fire in fluorine. Crystals of silicon, when brought into the gas, spontaneously inflame, and burn with brilliancy. All of the metals are acted upon by fluorine; some, when finely divided, undergoing spontaneous inflammation when thrown into the gas. Even gold and platinum are attacked by fluorine, especially if gently warmed; its action upon the latter metal being seen by the corrosion of the apparatus, and especially the positive electrode employed in its preparation.

FIG. 90.

Organic compounds are attacked by fluorine with violence, and often inflamed.

When fluorine is cooled to a temperature about – 187° (*i.e.* a few degrees below the temperature of boiling oxygen, obtained by boiling the oxygen under slightly reduced pressure) it condenses to the liquid state.* Liquid fluorine is a mobile yellow liquid, resembling liquid chlorine. Its specific gravity is 1.14. It is without action upon silicon, phosphorus, sulphur, or glass; it can therefore be produced and contained in glass vessels. Even at this low temperature, however, fluorine attacks hydrogen and hydrocarbons. When cooled by liquid hydrogen it forms a pale yellow solid, melting at −223°. On cooling the solid to −252° it loses its yellow colour and appears perfectly white.

HYDROFLUORIC ACID (*Hydrogen Fluoride*).

Formula, HF. Molecular weight=20.01. Density=10.

Modes of Formation.—(1.) Hydrofluoric acid is produced when powdered calcium fluoride (fluor spar) is acted upon by strong sulphuric acid—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

This method is employed for the commercial preparation of aqueous solutions of hydrofluoric acid. The mixture of fluor spar and sulphuric acid is gently warmed in a leaden retort, and the gaseous acid passed into water contained in leaden bottles. This aqueous acid is sent into the market in gutta-percha bottles.

(2.) The anhydrous acid is prepared by heating hydrogen potassium fluoride (acid potassium fluoride) in a platinum retort. The double fluoride of potassium and hydrogen splits up into normal potassium fluoride and hydrofluoric acid—

$$HF,KF = KF + HF.$$

For this purpose the perfectly dry double fluoride is placed in a platinum retort, which is screwed to a platinum condensing arrangement, as seen in Fig. 91. The wooden trough through which the long tube passes is filled with a freezing-mixture, and the platinum bottle is also surrounded by a similar mixture.

Properties.—Anhydrous hydrofluoric acid is a colourless, limpid, strongly fuming liquid, which boils at 19.5°. It has a powerful affinity for water, and can only be preserved in perfectly stoppered platinum vessels, which are kept in a cool place. The acid at once attacks gutta-percha. Gore found that the anhydrous acid was without action upon glass.

Pure hydrofluoric acid is an extremely dangerous substance to manipulate; its vapour, even when diluted with air, has a most

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* Moissan, May 1897.

irritating and injurious effect upon the respiratory organs, and if inhaled in the pure state causes death.

A single drop of the liquid upon the skin causes the most painful ulcerated sores, accompanied by distressing aching pains throughout the whole body. The metals potassium and sodium dissolve in pure hydrofluoric acid, with the formation of fluorides and evolution of hydrogen.

At temperatures above 88° the vapour-density of hydrofluoric acid corresponds to the formula HF. As the temperature is lowered the molecules aggregate together, and the density of the vapour steadily rises, until at a few degrees above the boiling-point it approaches what would be required for molecules of H_3F_3. At about 32° the density is 20; but whether this signifies the existence of molecules having the composition H_2F_2, or whether it merely represents a certain mixture of more complex molecules, H_nF_n, with molecules of HF, has not been definitely determined.

FIG. 91.

Gaseous hydrofluoric acid rapidly attacks glass, and it is largely employed for etching purposes, both for obtaining designs upon glass and for the purpose of etching graduations upon glass measuring instruments. The object to be etched is first coated with wax, and the design or other marks cut upon the wax by means of a pointed steel tool. In this way the surface of the glass is laid bare in parts, and on exposing the object to the action of the acid, either as gas or aqueous solution, the glass is rapidly eaten into, where the surface has been exposed. Its action upon glass is due to the readiness with which it attacks silicates, the fluorine combining with the silicon to form silicon tetrafluoride—

$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

Crystallised silicon, when gently heated, takes fire in gaseous hydrofluoric acid, giving silicon fluoride and hydrogen.

Hydrofluoric acid is extremely soluble in water, forming a strongly acid corrosive liquid, which readily dissolves many of the metals with evolution of hydrogen—

$$Fe + 2HF = FeF_2 + H_2.$$

Silver and copper are also dissolved by this acid.

CHLORINE.

Symbol, Cl. Atomic weight = 35.45. Molecular weight = 70.90.

History.—Chlorine was discovered by Scheele (1774), but was regarded by him as a compound substance. He applied to it the name of *dephlogisticated marine acid air*, having obtained it by the action of hydrochloric acid upon ores of manganese. The belief that chlorine was a compound of oxygen and hydrochloric acid was generally held until Davy's time, and gave rise to the name of *oxymuriatic acid.*

The elementary nature of chlorine was proved by Davy (1810), who gave to it the name *chlorine*, in allusion to the greenish-yellow colour of the gas.

Occurrence.—In the uncombined condition chlorine does not occur in nature. In combination with metals, as chlorides, chlorine is very abundant, the commonest chloride being sodium chloride (common salt).

Many of the salts found in the Stassfurt deposits consist largely of chlorides (see Alkali Metals). Chlorides of the alkali metals are also found in animal secretions and in certain plants. Chlorine occurs in combination with hydrogen, as hydrochloric acid, in volcanic gases, and also in the gastric juice.

Modes of Formation.—(1.) When hydrochloric acid is poured upon manganese dioxide, and the mixture kept cool, a dark-brown solution is obtained, which rapidly decomposes at a slight rise of temperature with the evolution of chlorine.

It has not yet been clearly established whether this brown solution consists of the compound $MnCl_4$ or Mn_2Cl_6, formed according to one of the equations—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

or—

$$2MnO_2 + 8HCl = Mn_2Cl_6 + Cl_2 + 4H_2O.$$

When this dark-brown solution is gently warmed, the higher chloride breaks up into manganous chloride ($MnCl_2$) and chlorine; the complete reaction being expressed by the equation—

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

The experiment is conveniently carried out in the apparatus seen in Fig. 92. The mixture of manganese dioxide and hydrochloric acid is gently heated in a large flask, and the gas, after being passed through water in the Woulf's bottle, may be collected by downward displacement, as shown in the figure.*

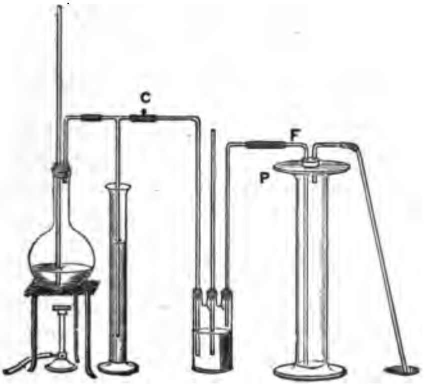

FIG. 92.

(2.) Instead of employing hydrochloric acid, the materials from which this compound is prepared, namely, sodium chloride and sulphuric acid, may be used. Thus, if a mixture of sodium

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* See Experiment 154, "Chemical Lecture Experiments," new ed.

chloride, manganese dioxide, and sulphuric acid be gently warmed, chlorine is readily evolved—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

It will be seen that by this reaction the whole of the chlorine contained in the reacting compounds is evolved as gas, while in the former case a part of it remains in combination with the manganese.

(3.) Many other highly oxygenised compounds, when acted upon by hydrochloric acid, evolve chlorine ; thus, when crystals of potassium dichromate are drenched with hydrochloric acid and the mixture heated, a rapid stream of chlorine takes place, thus—

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2.$$

(4.) When crystals of potassium chlorate are similarly treated, a mixture of chlorine and chlorine peroxide is evolved, even without the application of heat—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + 9Cl.$$

(5.) Red lead (Pb_3O_4), when treated with hydrochloric acid, reacts in a manner similar to manganese dioxide and many other peroxides. In the case of lead, however, there is no intermediate chloride formed—

$$Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2.$$

(6.) **Manufacturing Processes — Deacon's Process.** — This method for the preparation of chlorine is by the oxidation of the hydrogen in hydrochloric acid by *atmospheric* oxygen. It will be seen that in the foregoing methods the oxidation of this hydrogen is carried on at the expense of the oxygen contained in either the metallic peroxide or the highly oxygenated salt used ; in the Deacon process atmospheric oxygen is made use of. When a mixture of gaseous hydrochloric acid and oxygen is heated, a slight decomposition takes place ; but if these gases be heated in the presence of a third substance which acts as a catalytic agent, the decomposition of the hydrochloric acid is much more readily effected. The catalytic agent employed in the Deacon process is cuprous chloride (Cu_2Cl_2). This substance is capable of taking up an additional quantity of chlorine, and of being converted into cupric chloride ($CuCl_2$), thus—

$$Cu_2Cl_2 + Cl_2 = 2CuCl_2.$$

If, therefore, a mixture of hydrochloric acid and oxygen be passed over fragments of pumice impregnated with cuprous chloride contained in a tube which is heated to dull redness, the hydrochloric acid will be decomposed. We may suppose that the affinity of oxygen for the hydrogen in hydrochloric acid is unable to overcome the affinity existing between the hydrogen and chlorine, but that the additional pull exerted upon the molecules of hydrochloric acid by the cuprous chloride is sufficient to disturb the equilibrium and rupture the molecule—

$$O \leftarrow \begin{matrix} H\vdots Cl \\ H\vdots Cl \end{matrix} \rightarrow Cu_2Cl_2.$$

The result of the action being $H_2O + 2CuCl_2$.

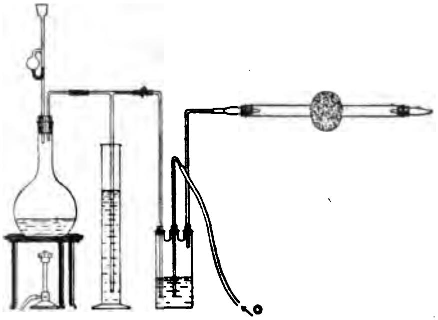

FIG. 93.

At the temperature at which the reaction is carried on, however, the compound $CuCl_2$ cannot exist; two molecules of it are converted into one of Cu_2Cl_2, and a molecule of chlorine is evolved. The final result, therefore, of the reaction may be thus expressed—

$$O + 2HCl + Cu_2Cl_2 = H_2O + Cl_2 + Cu_2Cl_2.$$

In reality the action is rather more complex, there being an intermediate compound formed by the combination of cuprous chloride with oxygen. This oxychloride of copper then acts upon the hydrochloric acid, as seen in the following equations :—

$$(1)\ Cu_2Cl_2 + O = Cu_2OCl_2.$$
$$(2)\ Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O.$$
$$(3)\ 2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

This reaction may be made on a small scale by means of the apparatus shown in Fig. 93. Hydrochloric acid is generated from salt and sulphuric acid in the flask, and a stream of the gas passed through the Woulf's bottle, into which also enters a stream of oxygen. The mixed gases are then passed through the bulb-tube, containing fragments of pumice which have previously been soaked in a solution of cupric chloride and dried. On heating the bulb by means of a Bunsen flame, chlorine will issue from the end of the tube. When chlorine is manufactured on an industrial scale by the Deacon process, the mixture of hydrochloric acid and air (in the proportion of four volumes of the latter to one volume of hydrochloric acid) is drawn by means of a Root's blower first through iron pipes, which are heated to a temperature of about 500°, and then the hot gases pass on through the *decomposer*. This consists of a cylinder of cast iron containing masses of broken brick or burnt clay impregnated with cupric chloride, and so arranged that the gases are drawn through the mass.

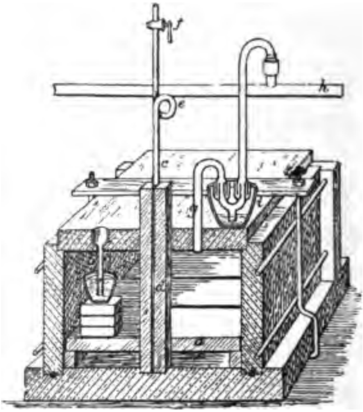

FIG. 94.

The gas leaving the decomposer consists of a mixture of chlorine, undecomposed hydrochloric acid, and atmospheric nitrogen and oxygen. By passing them through water, the hydrochloric acid is removed, and the chlorine is usually converted at once into bleaching-powder.

The process by which chlorine is usually made on a manufacturing scale is by the action of hydrochloric acid upon manganese dioxide. The best ore for the purpose is pyrolusite. The process is conducted in stills made of thick slabs of stone, usually "Yorkshire flag," which are fitted and luted together, and securely bound by cast-iron clamps. Fig. 94 shows such a chlorine still, represented as cut across the centre.

The charge of *manganese* is placed upon the false bottom *a*, and the acid is run in through the funnel tube *b*, which, dipping into a small pot, does not allow the gas to escape. As the action begins to slacken, steam is cautiously blown in from time to time. The chlorine escapes by the pipe *g*, and passes from thence into the main *h*.

The reaction that goes on in the still is the same as that given above in the first mode of formation, except that as pyrolusite is not pure MnO_2, small quantities of other compounds are formed. The following analysis, by Black, of *still-liquor* from stone stills, shows the general composition of this substance :—

$MnCl_2$	10.5700
Al_2Cl_6	0.6200
Fe_2Cl_6	0.4551
HCl (undecomposed)	6.6220
H_2O	81.7329
	100.0000

(7.) **The Weldon Process,** although indirectly a method for making chlorine, is in reality a process for recovering the manganese contained in the still-liquors as manganous chloride, and of reconverting it into available manganese dioxide. The manganese so recovered, however, is again utilised for the preparation of chlorine by the decomposition of a further quantity of hydrochloric acid. The essence of the process is the following :—The *still-liquor* is mixed with ground chalk, or limestone dust, in large tanks or wells, and the mixture thoroughly stirred by agitators. One of these wells, A, is shown in the diagrammatic figure. By this operation the free acid is neutralised, and the iron precipitated as hydrated oxide. The neutral liquor, consisting of manganous chloride and calcium chloride, is then pumped into large tanks, where it is allowed to settle; one of these "settlers," B, is shown in the figure. By means of a pipe upon a swivel-joint, *f*, the clear liquid from the settler can be drawn off without disturbing the sediment, and run into the oxidiser C. The oxidiser is merely a flat-bottomed iron cylinder, open at the top. Milk of lime from the tank E, where lime and water are stirred together, is pumped into the oxidiser as required.

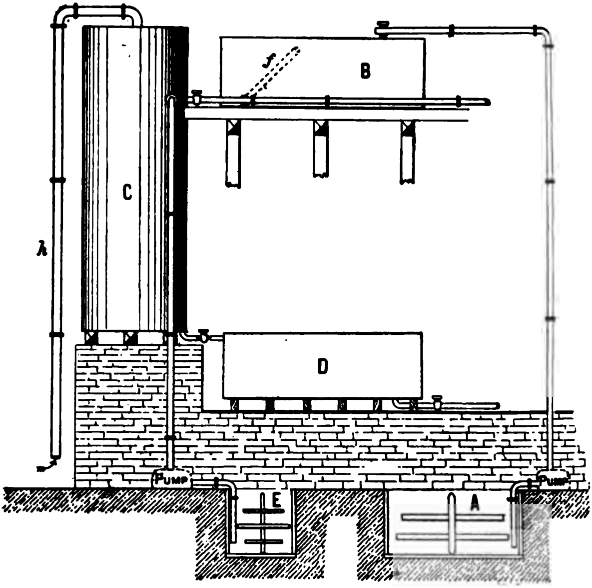

FIG. 95.

The milk of lime is added in quantity more than sufficient to precipitate the manganese as manganous hydroxide, MnH_2O_2. Into this mixture, which consists of manganous hydroxide and calcium hydroxide (milk of lime) in suspension, and to a smaller extent in solution in the calcium chloride which is present, a stream of compressed air is forced by means of the pipe *h*, which passes to the bottom of the oxidiser, where it ends in perforated branches. During this process the manganese becomes oxidised and is converted mainly into calcium manganite, a compound of manganese dioxide with calcium oxide, CaO,MnO_2, or $CaMnO_3$. By a further addition of the neutral liquor from tank B, and by raising the temperature within the oxidiser by injecting steam, a portion of the calcium manganite is converted into a compound having the composition $CaO,2MnO_2$.

When the operation is complete, the contents of the oxidiser are run out into a series of tanks called *mud settlers*, of which one is shown at D in the figure. The product here settles as a thin black mud, known as the *Weldon mud;* and this is ultimately drawn from the settlers, and run direct into chlorine stills, where it is at once treated with hydrochloric acid for the preparation of chlorine. The Weldon stills are similar to the ordinary chlorine stills, but are much larger, and usually octagonal in shape.

(8.) **Electrolytic Methods.**—Of late years, since the application of electricity on a commercial scale has become possible, manufacturing processes for obtaining chlorine by the electrolysis of a solution of common salt have begun to compete with the older methods. By the electrolysis of brine, the sodium chloride is separated into its two elements ; the chlorine is evolved at the anode, and the sodium which is liberated at the cathode there acts upon the water present, generating sodium hydroxide (see Caustic Soda ; also Sodium Carbonate).

Properties.—Chlorine is a greenish-yellow coloured gas, with a strong suffocating smell. It is quite irrespirable, and if inhaled in the pure state causes death. Even when largely diluted with air it is extremely disagreeable and injurious, as it acts rapidly upon the mucous membranes of the nose and throat, causing irritation and inflammation, which usually result in severe catarrh. A few bubbles of chlorine allowed to escape and diffuse into the air of a room give to the air a distinct and rather pleasant smell. Chlorine is an extremely heavy gas, being $\frac{35.45}{14.44} = 2.45$ times heavier than air. One litre of the gas, measured under the standard conditions of temperature and pressure, weighs 3.168 grammes. The density of chlorine, taken at all temperatures, does not exactly agree with that which is required for the molecular formula Cl_2. At temperatures above 1200° the density is markedly less than theory demands, showing that partial dissociation of the chlorine molecules into single atoms has taken place. (Compare Bromine and Iodine.)

On account of its heaviness, chlorine is readily collected by displacement; it cannot be collected over mercury, as it attacks that metal, and in water it is considerably soluble. It may, however, be collected over a strong brine, as it is much less soluble in this solution than in water.

Chlorine is not inflammable, but it supports the combustion of many burning bodies. It is possessed of such extremely powerful chemical affinities that it acts upon a large number of substances at ordinary temperatures, and in many cases the combination is sufficiently energetic to result in the inflammation of the bodies. Phosphorus, when introduced into chlorine, first melts and then spontaneously inflames, burning with a somewhat feeble light to form phosphorus trichloride (PCl_3) and phosphorus pentachloride (PCl_5). The elements arsenic and antimony, when finely powdered and dusted into a vessel of chlorine at once take fire and burn, forming their respective chlorides. Many metals, when finely divided, or in the form of thin leaf, such as ordinary Dutch metal, instantly take fire when brought into chlorine. If a quantity of sodium be heated in a deflagrating spoon until it begins to burn in the air, and be then plunged into chlorine, the sodium continues to burn in the gas with dazzling brilliancy, forming sodium chloride.

Although under ordinary circumstances chlorine unites with metals with great readiness, it has been shown that this action will not take place if the chlorine be absolutely dry. Thus, if chlorine which has been completely freed from aqueous vapour be passed into a tube containing bright metallic sodium, and the tube sealed, the sodium not only remains bright and unaffected by the gas, but may even be melted in the atmosphere of chlorine without any action taking place. Similarly, dry chlorine, when allowed to enter a flask filled with Dutch metal, has no action upon it; but upon the introduction of the smallest trace of moisture the metal at once takes fire.* These facts are of the same order as those mentioned in connection with oxygen (see page 191).

Chlorine is not capable of direct combination with carbon; ordinary combustibles, therefore, which consist of hydrocarbons, burn in chlorine by virtue of the combination of their hydrogen with the gas, and they burn with a lurid smoky flame, owing to the elimination of their carbon in the form of soot. A burning taper or

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* See Experiments 174, 175, "Chemical Lecture Experiments," new. ed.

ordinary gas flame when introduced into chlorine burns in this manner, emitting a dense smoke and forming fumes of hydrochloric acid.

Chlorine has a most powerful affinity for hydrogen; a jet of hydrogen burns freely in chlorine, with the formation of hydrochloric acid. A mixture of hydrogen and chlorine unites with explosion on the application of a flame. This combination takes place also under the influence of light (see Hydrochloric Acid). The affinity shown by chlorine for hydrogen is seen in its action upon many of the compounds of hydrogen and carbon. If one volume of ethylene (C_2H_4) be mixed with two volumes of chlorine, and the mixture ignited, the carbon is instantly thrown out of combination as a black smoke, while the hydrogen unites with the chlorine, forming a cloud of hydrochloric acid. Similarly, if a liquid hydrocarbon, such as turpentine ($C_{10}H_{16}$), be poured upon a piece of filter paper, and the paper be thrust into a jar of chlorine, instant inflammation takes place, with deposition of a large quantity of carbon.

Chlorine possesses strong bleaching properties, which depend upon its power of combining with hydrogen, for it is an essential condition that water shall be present. The chlorine unites with the hydrogen of the water, and the liberated oxygen oxidises the colouring matter. If chlorine be bubbled into liquids coloured with any vegetable colouring matter, or if a dyed rag be dipped into chlorine water, the colour will be rapidly discharged. Ordinary writing-ink (which usually consists of a compound of iron with tannic and gallic acids) is readily bleached by chlorine; while printer's ink, which consists mainly of carbon, in the form of lampblack, is not acted upon by this gas. If, therefore, a piece of printed paper be brushed over with writing-ink so as to completely obliterate the print, and the blackened paper be immersed in chlorine water, the writing-ink will be rapidly bleached away, leaving the print unchanged.

The bleaching power of chlorine constitutes its most valuable property from an industrial point of view; the chlorine for this purpose is combined with lime to form the substance known as bleaching-powder (see Calcium Compounds).

Chlorine is soluble in water to a considerable extent. One volume of water at 10° absorbs 3.0361 volumes of chlorine measured at 0° and under 760 mm. pressure. This solution, known as chlorine water, has the same colour as the gas, and smells strongly of chlorine. If exposed to the air, the chlorine rapidly diffuses out of the solution. Chlorine water cannot be preserved for any length of time, as it slowly undergoes decomposition, the chlorine combining with the hydrogen of the water, forming hydrochloric acid, which remains in solution, and the oxygen being liberated, thus—

$$H_2O + Cl_2 = 2HCl + O.$$

This action, which proceeds slowly under ordinary conditions, is greatly accelerated by the influence of light, and if exposed to direct sunlight the decomposition is very rapid.

If chlorine water be cooled to within one or two degrees of the freezing-point of water, or if chlorine be passed into ice-cold water, a solid crystalline compound of chlorine with water is deposited. This substance is termed *chlorine hydrate*, and has a composition expressed by the formula $Cl_2,10H_2O$. The compound is very unstable, and when exposed to the air it melts and rapidly gives off chlorine. If the crystals are quickly freed from adhering water, and are then sealed up in a glass tube, they may be heated to a temperature of 38° before being decomposed. Faraday made use of this compound in order to obtain liquefied chlorine. A quantity of the hydrate was sealed up in one limb of a bent tube and was gently warmed, the compound dissociated into water and chlorine, and the internal pressure caused the condensation of the chlorine to the liquid condition.

Liquid Chlorine.—Under the ordinary atmospheric pressure, chlorine may be liquefied by lowering its temperature to $-34°$.

At a temperature of 0° the pressure required to effect its liquefaction is equal to six atmospheres. When, therefore, the liquid is obtained by heating the crystalline hydrate, as in Faraday's method, one limb of the tube should be cooled by being placed in ice.

The critical temperature of chlorine is 141°, and the pressure required to effect its liquefaction at that point, or its critical pressure, is 84 atmospheres (see Liquefaction of Gases).

Liquid chlorine has a bright golden-yellow colour, entirely free from the greenish tint possessed by the gas. Its specific gravity is 1.33, and it boils at $-33.6°$. When cooled to a temperature of $-102°$, it freezes to a yellow crystalline mass. Liquid chlorine is now an article of commerce. It is contained in iron bottles lined with lead, and is largely exported in this form, for use in the extraction of gold, to parts of the world where the carriage of the plant and materials necessary for generating large quantities of chlorine would be attended with great difficulties.

HYDROCHLORIC ACID (*Hydrogen Chloride*).

Formula, HCl. Molecular weight=36.46. Density=18.23.

History.—In solution in water this compound was known to the early alchemists, and the mixture of this solution with nitric acid constituted the valued liquid known as *aqua regia.* The preparation of hydrochloric acid from common salt is associated with the name of Glauber (1650), who obtained it by the action of sulphuric acid upon sodium chloride (common salt). Gaseous hydrochloric acid was first collected and examined by Priestley, who collected it over mercury in the mercurial pneumatic trough invented by him. He named the gas *marine acid air.*

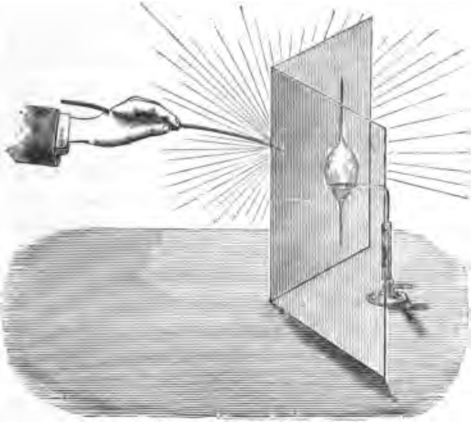

FIG. 96.

Occurrence.—Gaseous hydrochloric acid is evolved in considerable quantities from volcanoes during active eruption.

Modes of Formation.—(1.) Hydrochloric acid may be synthetically produced directly from its elements ; thus, this compound is formed when a jet of hydrogen is caused to burn in an atmosphere of chlorine. If a mixture of chlorine and hydrogen be ignited, the union takes place instantaneously with explosion, and hydrochloric acid is produced. The union of hydrogen with chlorine will also take place under the influence of light; thus, if a mixture of these two gases be exposed to even diffused daylight for a few hours the greenish colour imparted to the mixture by the chlorine will gradually disappear, and on examination it is found that the tube contains hydrochloric acid. This combination, which is only gradual when the mixture is exposed to diffused daylight, becomes explosively sudden if the mixed gases are exposed to direct sunlight, or any artificial light which is rich in rays of high refrangibility—the so-called *actinic* rays. If, therefore, a glass vessel be filled with a mixture of these gases in equal volumes, and the mixture be placed in bright sunshine, a violent explosion will result, and hydrochloric acid will be produced. This phenomenon is best illustrated by filling small thin glass bulbs with a mixture of the two gases obtained by the electrolysis of aqueous hydrochloric acid. The bulbs when filled can be hermetically sealed before the blowpipe without causing the combination of the gases,* and if kept in the dark may be preserved indefinitely.

On exposing one of these bulbs to the light of burning magnesium the combination of the two gases instantly takes place, with a sharp explosion which shatters the bulb to powder. The bulb should therefore be screened, as shown in Fig. 96.

The rays of light which are capable of causing this combination are those which compose the blue and violet end of the spectrum; if these particular rays are absorbed from the light by means of ruby glass, the mixture of gases may be exposed to the red light so obtained without any action taking place.†

FIG. 97.

The combination of chlorine with hydrogen is not attended by any alteration in volume; one volume of chlorine combines with one volume of hydrogen, and the resultant hydrochloric acid occupies two volumes. This may be readily proved by filling a stout glass tube, provided with a stop-cock at each end, with a mixture of the two gases in exactly equal volumes, and causing them to combine either

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* See Experiment 178, "Chemical Lecture Experiments," new ed.

† Ibid., p. 93.

by the influence of light or by the passage of an electric spark by means of the platinum wires sealed into the tube (Fig. 97). On opening one of the stop-cocks under mercury it will be seen that no mercury is drawn in, neither does any gas pass out from the tube, thus showing that the union has taken place without any alteration in the volume. If one of the cocks be now opened beneath water, the hydrochloric acid which has resulted from the union of the hydrogen and chlorine, being extremely soluble in water, the liquid will rush up into the tube and completely fill it, showing that no free hydrogen or chlorine remains in the tube.

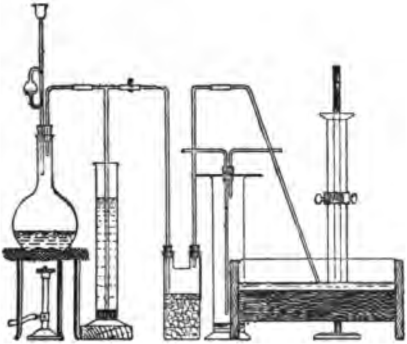

FIG. 98.

(2.) For all ordinary purposes, hydrochloric acid is always obtained by the action of sulphuric acid upon sodium chloride. For laboratory uses the apparatus seen in Fig. 98 may be conveniently employed. Sulphuric acid, previously diluted with rather less than its own volume of water, is placed in the flask, and a quantity of common salt is added. On the application of a gentle heat a steady stream of gas is evolved, which may be dried by being passed through the tubulated bottle, containing pumice moistened with strong sulphuric acid. The gas is then collected either over mercury or by displacement. The reaction which takes place is expressed by the equation—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

If strong sulphuric acid be employed along with an excess of salt, both of the atoms of hydrogen can be displaced from the acid; and instead of the hydrogen sodium sulphate there is formed the normal sodium sulphate—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

A much higher temperature is necessary in order to complete the reaction indicated by this equation.

Properties.—Hydrochloric acid is a colourless gas with a choking, pungent odour. In contact with the moist air it forms dense fumes, consisting of minute globules of a solution of the gas in the atmospheric aqueous vapour. Hydrochloric acid does not burn, neither does it support ordinary combustion.

It is heavier than air, its specific gravity being—

$$\frac{18.23}{14.44} = 1.26 \text{ (air} = 1).$$

Hence the gas is readily collected by displacement. One litre of the gas weighs 18.185 criths.

Hydrochloric acid is extremely soluble in water; 1 volume of water at 0° and under a pressure of 760 mm. is capable of dissolving 503 volumes of gaseous hydrochloric acid, measured at 0° and 760 mm. As the temperature rises the solubility diminishes, as seen by the following table:—

Temperature.	Coefficient of Absorption.
0°	503
30°	411
50°	364

The solubility of hydrochloric acid may be illustrated by completely filling a large globular flask with the gas, by displacement, the flask being provided with a long tube passing through the cork, as seen in Fig. 99. On opening this tube beneath water, the gas begins to dissolve, and the liquid rises slowly in the tube until it reaches the top. As soon as the first few drops enter the globe, they rapidly absorb the gas, thereby causing a partial vacuum in the vessel, so that the water is driven up the tube with considerable force, forming a fountain, which continues until the globe is nearly filled with liquid. If the water in the dish is rendered blue by the addition of litmus solution, the acid nature of the solution of the gas will be evident by the reddening of the liquid as it enters the globe.

When a weak aqueous solution of hydrochloric acid is boiled it loses water and becomes stronger; while, on the other hand, if a strong solution be heated, it loses gas and becomes weaker, until in both cases an acid containing 20.24 per cent. of HCl is produced which boils at 110°. This strength of acid corresponds to a composition expressed by the formula $HCl + 8H_2O$, and it was at one time supposed to represent a definite compound. Roscoe and Dittmar have shown, however, that, as with nitric acid, the composition of the liquid which boils at a constant temperature is simply a function of the pressure. (Compare Nitric Acid, page 239.)

The strongest aqueous solution of hydrochloric acid at 15° C. has a specific gravity of 1.212, and contains 42.9 per cent. of HCl.

Hydrochloric acid gas is readily liquefied by pressure. At a temperature of 10° a pressure of 40 atmospheres will effect its liquefaction. If the temperature be lowered to $-16°$, the same result is obtained by a pressure of 20 atmospheres. The critical temperature of hydrochloric acid is 52.3°.

Condensed hydrochloric acid is a colourless liquid. Gore has shown that this liquefied acid is without action on most of the metals which are readily dissolved by the aqueous acid.

FIG. 99.

The composition of hydrochloric acid may be experimentally proved by a number of methods. It may be shown synthetically by the volumetric experiment referred to above (page 364).

The volumetric proportion of hydrogen contained in the gas may be shown by means of sodium amalgam. The sodium in the amalgam acts upon the hydrochloric acid, combining with the chlorine, and liberating the hydrogen—

$$2Na + 2HCl = 2NaCl + H_2.$$

For this purpose gaseous hydrochloric acid is introduced into one limb of the U-shaped eudiometer (Fig. 100), and its volume indicated by means of a ring upon the tube, the mercury being level in both limbs. A second ring marks exactly half the volume. A quantity of liquid sodium amalgam is then poured into the open limb until it is completely filled, and on being closed by the thumb the tube can be inverted so as to decant the gas into this limb. After being bubbled once or twice through the amalgam, the gas is again returned to its former place; and by drawing mercury from the branch tube, the levels in each limb can be again adjusted, when it will be found that the gas remaining in the tube occupies the space exactly down to the upper ring, that is to say, two volumes of hydrochloric acid contain one volume of hydrogen. That the gas is hydrogen can be shown by again filling up the open limb with mercury, and driving the gas out of the stop-cock, where it can be inflamed as it escapes.

FIG. 100.

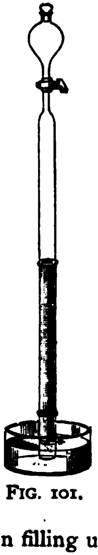

FIG. 101.

FIG. 102.

The fact that hydrochloric acid contains the same volume of chlorine as of hydrogen may also be demonstrated by collecting the mixed gases, evolved by the electrolysis of the aqueous acid, in a long tube provided with a stoppered funnel, as shown in Fig. 101.

The gases may be collected over a saturated solution of salt in water, and the tube filled to the lower ring. On allowing a solution of potassium iodide to enter by means of the funnel, the chlorine is absorbed with the liberation of iodine, which partially dissolves and partly separates as a solid. When the absorption of the chlorine is complete, the water will have risen to the second band placed half-way up the tube, showing that one-half of the gaseous mixture consists of chlorine. The former experiment proved that hydrochloric acid contained half its volume of hydrogen, therefore the two elements, in uniting to form this compound, do so in equal volumes and without any contraction in volume.

When aqueous hydrochloric acid is subjected to electrolysis, the hydrochloric acid is decomposed, hydrogen being evolved at the negative electrode and chlorine at the positive. At first the liberated chlorine is dissolved in the solution, but after the liquid has become saturated with the gas, the whole of the chlorine is liberated. By conducting this decomposition in the apparatus seen in Fig. 102, and continuing the passage of the electric current until the liquid in one limb is saturated with chlorine before closing the stop-cocks, it will be seen, when the gases are collected in the tubes, that they are evolved in equal volumes.

The Manufacture of Hydrochloric Acid.—The aqueous solution of hydrochloric acid is an object of commercial manufacture, which is carried out on an enormous scale. It is obtained by the decomposition of common salt by means of sulphuric acid, according to the reaction—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Formerly hydrochloric acid was a waste product obtained in the manufacture of sodium carbonate by the method known as the *Leblanc process*, the first stage in this process being the conversion of sodium chloride into sodium sulphate by the action upon it of sulphuric acid. The hydrochloric acid evolved as gas in this reaction was allowed to escape into the atmosphere. The nuisance caused by this acid gas being thrown into the air, ultimately resulted in the "Alkali Act," which compelled manufacturers to absorb this waste acid. Since that time the Leblanc process for the manufacture of sodium carbonate has had a formidable rival in another method, known as the *ammonia-soda process* (see Sodium Compounds), which would probably have completely driven the older method out of the field, but for the commercial value of the hydrochloric acid which is obtained as a secondary product in the Leblanc process. The hydrochloric acid, therefore, which formerly was thrown away as a waste product, is now the salvation of the process, and the utmost care is taken to prevent any of it from escaping, not now by compulsion of the Alkali Act so much as from purely economic reasons.

The charge of salt and sulphuric acid is heated in an enormous hemispherical cast-iron pan, built into a brickwork chamber, so that it can be heated by a fire beneath, and so that the evolved gas can be conveyed away by brick or earthenware flues. The gas evolved by the reaction is led into towers which are filled with coke or bricks, and down which water is made to percolate, the water being caused to flow equally over the mass by means of special distributing contrivances. As the gaseous hydrochloric acid passes up the towers and meets the descending stream of water it is entirely dissolved, and the aqueous acid becomes nearly saturated as it reaches the bottom of the tower.

In works where the condensers or towers are not of great height, it is usual either to cool the gas before admitting it into the towers, or to pass it through a series of jars resembling gigantic Woulf's bottles (Fig. 103).

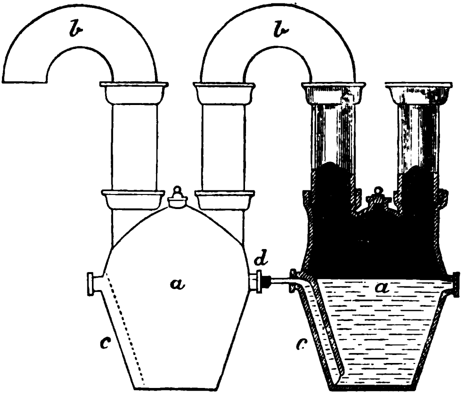

FIG. 103.

The water in these bottles is made to flow steadily from one to the other by the side pipes *c*, *c* (in the direction from left to right), while the gas passes through the system in the opposite direction. In this way a constantly changing surface of water is exposed to the gas, and a very strong solution is obtained.

Commercial hydrochloric acid is generally yellow in colour, owing to the presence of iron as an impurity; and it is always liable to contain sulphuric acid, free chlorine, arsenic, and sometimes sulphur dioxide. This aqueous solution of hydrochloric acid is also known under the names of "spirits of salt" and muriatic acid.

OXIDES AND OXYACIDS OF CHLORINE.

The elements oxygen and chlorine have never been made to unite together directly: three compounds, however, of these elements can be obtained b[illegible]irect methods; these are—

Chlorine monoxi[illegible]ochlorous anhydride)	Cl_2O.
Chlorine peroxide	ClO_2.
Chlorine [illegible]ptoxide	Cl_2O_7.

Three oxyacids are known, [illegible]z.:—

Hypochlorous acid	$HClO$.
Chloric acid	$HClO_3$.
Perchloric acid	$HClO_4$.

CHLORINE MONOXIDE (*Hypochlorous Anhydride*).

Formula, Cl_2O. Molecular weight = 86.90. Density = 43.45.

Mode of Formation.—This compound is obtained by passing dry chlorine over dry precipitated mercuric oxide contained in a glass tube, the temperature of which is not allowed to rise. The chlorine combines with the mercuric oxide, forming mercuric oxychloride, and chlorine monoxide is liberated—

$$2HgO + 2Cl_2 = HgO,HgCl_2 + Cl_2O.$$

Properties.—At ordinary temperatures chlorine monoxide is a pale yellow gas, without the greenish tint possessed by chlorine. Its smell strongly suggests chlorine, but is readily distinguishable from it. It is a very unstable compound, decomposing with more or less violence with moderate rise of temperature. When strongly cooled it is condensed to an orange-yellow coloured liquid, which boils at about −20°. This liquid is extremely unstable, exploding with great violence on the gentlest application of heat, and sometimes on merely being poured from one vessel to another. When exposed to direct sunlight it also explodes with violence.

Gaseous chlorine monoxide is considerably soluble in water, one volume dissolving about 100 volumes of the gas, forming hypochlorous acid—

$$Cl_2O + H_2O = 2HClO.$$

CHLORINE PEROXIDE.

Formula, ClO_2. Molecular weight = 67.45. Density = 33.72.

Modes of Formation.—(1.) By the action of sulphuric acid upon potassium chlorate—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2HKSO_4 + H_2O + 2ClO_2.$$

Finely powdered potassium chlorate is added little by little to concentrated sulphuric acid in a small retort. The salt dissolves with the formation of a reddish liquid, and if the temperature is not allowed to rise, no gas is evolved. On very cautiously warming the retort by means of warm water, taking care not to heat the glass above the level of the liquid in the retort, the chlorine peroxide is evolved.

(2.) A mixture of chlorine peroxide and carbon dioxide, in equal volumes, is obtained by heating a mixture of powdered potassium chlorate and oxalic acid to a temperature of 70° in a water-bath—

$$2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2.$$

(3.) Chlorine peroxide, mixed with chlorine, is evolved by the action of hydrochloric acid upon potassium chlorate—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + 3ClO_2.$$

This mixture of gases was formerly supposed to be a definite compound of oxygen and chlorine, and received the name of *euchlorine*.

Properties.—Chlorine peroxide is a heavy gas, with a deep yellow colour. It has an intensely unpleasant smell, and if inhaled, even when largely diluted with air, produces headache. The gas attacks mercury, and is soluble in water, so that it can only be collected by displacement. Chlorine peroxide is an extremely unstable compound, it is gradually resolved into its elements by the influence of light; the passage of an electric spark, or the introduction into it of a hot wire, causes it to decompose with violent explosion. It is a powerful oxidising compound; a piece of phosphorus introduced into the gas takes fire spontaneously. If a jet of sulphuretted hydrogen be lowered into a jar of chlorine peroxide, the sulphuretted hydrogen ignites spontaneously and continues burning in the gas.

Its oxidising action upon organic matter may be shown by liberating the gas in the presence of such a substance as sugar, by adding a drop of sulphuric acid to a mixture of powdered sugar and potassium chlorate. The chlorine peroxide, liberated by the action of the acid upon the chlorate, ignites the mixture, and the entire mass then bursts into flame.

When chlorine peroxide is strongly cooled it condenses to a dark red liquid, which is even more explosive than the gas.

Chlorine Heptoxide, Cl_2O_7.—This compound is obtained by the cautiously regulated action of phosphoric oxide upon perchloric acid,* whereby the elements of water are withdrawn from two molecules of the acid—

$$2HClO_4 - H_2O = Cl_2O_7.$$

The operation is attended with some danger, although the heptoxide when isolated is described as less unstable than either of the other oxides.

HYPOCHLOROUS ACID.

Formula, $HClO$.

Modes of Formation.—(1.) As already mentioned, this acid is formed when chlorine monoxide is dissolved in water.

(2.) It may readily be obtained in dilute solution by passing an excess of chlorine through water in which precipitated mercuric oxide is suspended—

$$HgO + H_2O + 2Cl_2 = HgCl_2 + 2HClO.$$

On distilling the liquid, the dilute acid passes over as a colourless distillate.

(3.) In dilute solution, hypochlorous acid may be obtained by the decomposition of a hypochlorite by a very dilute mineral acid, and subsequent distillation of the mixture; thus, if to a solution of calcium hypochlorite (obtained by treating bleaching-powder with water and filtering the solution) very dilute nitric acid be added and the solution distilled, a dilute colourless acid is obtained—

$$Ca(ClO)_2 + 2HNO_3 = Ca(NO_3)_2 + 2HClO.$$

(4.) This compound is also formed when a stream of chlorine is

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* Michael and Conn., *Am. Chem. Journ.*, 1900.

passed through water containing precipitated calcium carbonate in suspension—

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + CO_2 + 2HClO.$$

Properties.—Pure hypochlorous acid, free from water, has never been obtained. The acid produced by the solution in water of chlorine monoxide has a pale straw-yellow colour, and a very characteristic chlorous smell. Dilute solutions of this acid are moderately stable, while more concentrated solutions readily undergo spontaneous decomposition.

Hypochlorous acid is a powerful oxidising and bleaching agent, as it readily gives up its oxygen, and is resolved into hydrochloric acid—

$$HClO = HCl + O.$$

As an oxidising agent it is twice as effective as an equivalent quantity of chlorine in chlorine water, for two atoms of chlorine are here necessary for the liberation of one atom of oxygen—

$$Cl_2 + H_2O = 2HCl + O.$$

Hypochlorous acid is decomposed by hydrochloric acid with the evolution of chlorine—

$$HClO + HCl = H_2O + Cl_2.$$

It is also decomposed by silver oxide, oxygen being liberated—

$$Ag_2O + 2HClO = 2AgCl + H_2O + O_2.$$

The salts of hypochlorous acid may be obtained by the action of the acid upon the hydroxides of the metals ; thus—

$$HClO + KHO = KClO + H_2O.$$

The most important salt of this acid is *bleaching-powder* (see Calcium Salts).

CHLORIC ACID.

Formula, $HClO_3$.

Mode of Formation.—This compound is best obtained by decomposing barium chlorate with an exact equivalent of sulphuric acid, previously diluted with water—

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

The clear liquid is decanted from the precipitated barium sulphate, and is then concentrated by evaporation in vacuo.

The strongest acid that can be obtained still contains 80 per cent. of water. Attempts to concentrate it further result in its decomposition into free chlorine and oxygen, with the formation of perchloric acid and water.

Properties.—The strong aqueous acid has powerful oxidising properties; many organic substances, as wood or paper, are so rapidly oxidised by it that when the acid is dropped upon them they are frequently inflamed.

The acid even in dilute solution has strong bleaching powers.

The salts of chloric acid are far more stable than the acid, and some of them are of considerable technical importance. The chlorates are all soluble in water, and all yield oxygen on being heated. Chloric acid is a monobasic acid; the chlorates, therefore, have the general formula $M'ClO_3$ and $M''(ClO_3)_2$, where M′ and M″ stand for monovalent and divalent metals respectively.

Of all the chlorates, potassium chlorate, $KClO_3$, is by far the most important (see Potassium Compounds).

PERCHLORIC ACID.

Formula, $HClO_4$.

Mode of Formation.—Perchloric acid is best prepared by the action of strong sulphuric acid upon potassium perchlorate—

$$2KClO_4 + H_2SO_4 = K_2SO_4 + 2HClO_4.$$

Pure and dry potassium perchlorate is mixed with four times its weight of concentrated sulphuric acid, and the mixture gently distilled in a small retort. The distillate at first consists of perchloric acid; but as the operation proceeds a portion of the perchloric acid is decomposed into lower oxides of chlorine and water, and the latter, combining with the first portions of the distillate, forms a white crystalline compound, having the composition $HClO_4H_2O$. This body, when gently heated, gives off perchloric acid; it may, therefore, be employed for the preparation of the acid in a state of purity.

Properties.—Perchloric acid is a colourless, volatile, and strongly fuming liquid, having a specific gravity of 1.782 at 15°. It is an extremely powerful oxidising substance; a drop of the liquid allowed to fall upon paper, wood, or charcoal is instantly decomposed, sometimes with a violent explosion. In contact with the skin it produces most painful wounds ; when allowed to drop into water it produces a hissing sound, owing to the energy of the combination.

The salts of this acid are the perchlorates, of which the most important is potassium perchlorate ; they are all soluble in water.

Constitution of the Oxides and Oxyacids of Chlorine.—On the assumption that chlorine is a monovalent element, the constitution of these compounds may be thus represented :—

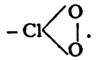
Chlorine monoxide, Cl – O – Cl. | Hypochlorous acid, Cl – O – H.
Chlorine peroxide, Cl – O – O –. | Chloric acid, Cl – O – O – O – H.
Perchloric acid, Cl – O – O – O – O – H.

It is possible, however, that in some of these compounds the chlorine functions as a trivalent element, and that these compounds have a constitution similar to the oxides and oxyacids of nitrogen, thus :—

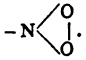
Chlorine monoxide, Cl – O – Cl.

Nitrogen monoxide, N – O – N.

Chlorine peroxide,



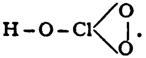
Nitrogen peroxide,



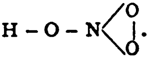
Hypochlorous acid, Cl – O – H.

Hyponitrous acid, N – O – H.

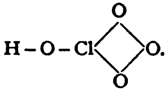
Chloric acid,



Nitric acid,



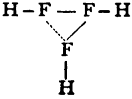
Perchloric acid,



There are several facts which point to the belief that not only chlorine, but also bromine and iodine, are capable of fulfilling the functions of a trivalent element. The existence, for example, of such a compound as trichloride of iodine, ICl_3, is difficult to explain on any other assumption than that iodine is here a trivalent element.

Indeed, from a consideration of the salts of periodic acids, some chemists are in favour of assigning to iodine even a still higher valency, and of regarding it as a heptad element in these compounds (see Periodates, page 394). The constitution of such molecules as those of hydrofluoric acid at low temperatures, namely, H_2F_2, or H_3F_3, or H_nF_n, and of the acid fluoride of potassium, HF,KF, is readily understood if we regard the fluorine as functioning in these compounds as a trivalent element, thus—

H – F = F – H ;



; H – F = F – K.

BROMINE.

Symbol, Br. Atomic weight=79.96. Molecular weight=159.92.
Vapour density=79.96.

History.—This element was discovered by Balard (1826), in the mother-liquor obtained after the crystallisation of salt from concentrated sea-water. He applied the name *bromine* (signifying a *stench*) to the element, in allusion to its unpleasant smell.

Occurrence.—Bromine is never found in the uncombined state in nature. In combination chiefly with the metals potassium, sodium, and magnesium, it occurs in small quantities in all sea-water, and more abundantly in many mineral waters and salt springs. The saline deposits of Stassfurt contain notable quantities of bromides, and the main supply of bromine for the market is manufactured from this source.

Modes of Formation.—(1.) Bromine may be obtained from a bromide by displacement with chlorine. If to a solution of magnesium bromide, chlorine water is added, the chlorine combines with the magnesium and the bromine is liberated—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

On distilling the liquid the bromine is driven off, and can be collected in a well-cooled receiver. The addition of any excess of chlorine results in the formation of bromide of chlorine, and is therefore to be avoided.

(2.) Bromine is readily obtained from potassium bromide by the action of manganese dioxide and sulphuric acid, a reaction exactly analogous to that by which chlorine is obtained from sodium chloride—

$$2KBr + MnO_2 + 2H_2SO_4 = MnSO_4 + K_2SO_4 + 2H_2O + Br_2.$$

The mixture is gently distilled from a retort into a receiver kept cold by means of ice.

(3.) **Manufacturing Methods.**—Practically all the bromine that is required at the present day is manufactured from crude carnallite obtained at Stassfurt (see Alkali Metals). This salt contains bromine combined with magnesium, the magnesium bromide forming about 1 per cent. of the magnesium chloride in the crude substance. The final mother-liquors from the manufacture of potassium chloride, and which were formerly run to waste, are found to contain about .25 per cent. of bromine as magnesium bromide, and these liquors are now utilised for the manufacture of bromine.

The bromine is liberated from its combination with magnesium, by means of chlorine. In some processes the mother-liquor is mixed with manganese dioxide and sulphuric acid in a stone vessel resembling an ordinary chlorine still. The magnesium chloride in the liquor is acted upon by the manganese dioxide and sulphuric acid with the evolution of chlorine, and this decomposes, the bromide present displacing the bromine—

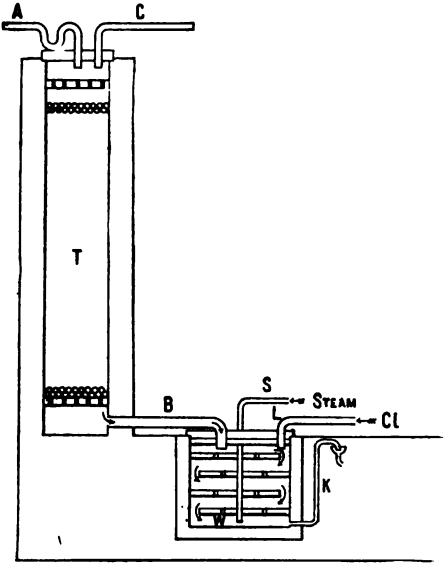


Fig. 104.

$$MgCl_2 + MnO_2 + 2H_2SO_4 = MnSO_4 + MgSO_4 + 2H_2O + Cl_2.$$
$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

The bromine that is driven out is condensed by means of a worm condenser.

Instead of the chlorine being generated within the mother-liquor, it is now more usually produced in a separate chlorine still, and passed into the liquor. Fig. 104 shows in diagrammatic form the method employed. The hot mother-liquor is admitted by the pipe A into the tower T, which is filled with earthenware balls, between which the liquid percolates. It leaves the tower by the pipe B, and flows into the tank W, which is provided with shelves in such a way that the liquid must circulate through it in the direction indicated by the arrows. The exit-pipe from this tank empties into a waste, placed at such a height that the tank is always nearly full. The liquid in the tank is kept at, or near, the boiling-point, by means of a current of steam blown in through S. Chlorine from a still is admitted by the pipe L, and passing into the tower by the pipe B, travels in an opposite direction to the current of liquid. As the chlorine passes up the tower it meets the descending mother-liquor, and decomposes the magnesium bromide contained in it with the liberation of bromine. The bromine vapour leaves the tower by the pipe C, and is conveyed to a worm (Fig. 105), where it is condensed. Any bromine which dissolves in the water in the tower is again expelled from solution by the steam as the liquid traverses the tank W, and is swept up into the tower by the current of chlorine. The condensed bromine as it leaves the worm is collected in a tubulated bottle, and any vapour which escapes con-

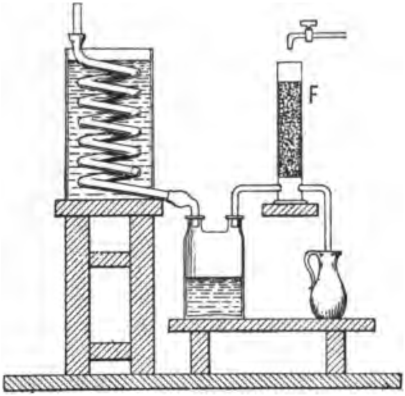


FIG. 105.

densation is arrested by the vessel F (Fig. 105). This tube is filled with iron borings, kept moist by the constant dropping of water upon them, and any bromine or bromide of chlorine is there converted into iron compounds, which are dissolved by the water, and flow away into the receiver. The bromine is purified by redistillation.

Just as in the case of chlorine, these older methods of manufacture seem destined to give place to electrolytic processes. The method now being introduced for the extraction of the bromine from the Stassfurt liquors depends upon the fact that when a solution containing a chloride and a bromide is submitted to electrolysis, the *bromine* is liberated first, before any chlorine escapes. Hence, by subjecting the liquors to electrolysis, under suitable conditions, the whole of the bromine is readily separated.

Properties.—Bromine is a heavy but mobile liquid of a deep reddish-brown colour. Except in extremely thin layers it is opaque. It is the only non-metallic element which is liquid at the ordinary temperature. Bromine boils at 59°, but being a very volatile liquid it gives off vapour rapidly at the ordinary temperature. A drop of bromine allowed to fall into a flask immediately evaporates and fills the vessel with a dark red-brown vapour. The specific gravity of the liquid at 0° is 3.188. At −7° bromine solidifies to a crystalline mass. Bromine has a powerful and disagreeable smell. When the vapour, largely diluted with air, is inhaled, it suggests chlorine by its smell and by its action upon the mucous membrane of the throat and nose; it has in addition, however, a most irritating action upon the eyes. It is very poisonous, and the liquid exerts a corrosive action upon the skin; it produces a yellow colour when brought in contact with starch.

The vapour-density of bromine, taken at moderately high temperatures, gradually becomes less than is demanded by the formula Br_2, showing that dissociation takes place. In the case of bromine this is more marked than with chlorine.

Bromine is soluble in water, imparting its own colour to the solution which is known as *bromine water*. 100 grammes of water at 0° dissolve 3.60 grammes of bromine. The solubility steadily diminishes as the temperature rises: at 20° it is 3.208, and at 30° it is 3.126.

When bromine water is cooled to 0° it deposits a crystalline hydrate similar in composition to the hydrate of chlorine, $Br_2,10H_2O$.

Bromine resembles chlorine in its chemical attributes; it combines directly with metals and many other elements, although with less energy than is exhibited by chlorine. A fragment of arsenic, for example, when dropped upon bromine, ignites and burns upon the surface of the liquid.

Like chlorine, it has bleaching properties, due to its power of combining with hydrogen.

HYDROBROMIC ACID (*Hydrogen Bromide*).

Formula, HBr. Molecular weight = 80.97. Density = 40.48.

Modes of Formation.—(1.) Hydrobromic acid can be obtained by the direct union of its elements. Bromine vapour and hydrogen, when mixed, do not combine under the influence of light; neither does such a mixture explode when a light is applied to it. The mixture, however, may be caused to burn, when hydrobromic acid is formed ; or, if the mixed gases be passed through a red-hot tube, the same result follows. A simple method of preparing hydrobromic acid synthetically consists in passing a mixture of hydrogen and bromine vapour over a spiral of platinum wire, maintained at a red heat by means of an electric current.*

(2.) The best method for the preparation of gaseous hydrobromic acid consists in dropping bromine upon red phosphorus which has been moistened with a small quantity of water, when tribasic phosphoric acid is formed, and hydrobromic acid is liberated—

$$P + 4H_2O + 5Br = H_3PO_4 + 5HBr.$$

We may suppose that in this reaction the bromides of phosphorus are formed and simultaneously decomposed, the action of water upon these compounds being thus expressed—

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr.$$
$$PBr_5 + 4H_2O = H_3PO_4 + 5HBr.$$

(3.) Hydrobromic acid may be obtained by the action of phosphoric acid upon potassium bromide—

$$3KBr + H_3PO_4 = K_3PO_4 + 3HBr.$$

(4.) If sulphuric acid be employed (as in the formation of hydrochloric acid from a chloride), free bromine is simultaneously pro-

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* See "Chemical Lecture Experiments," new ed., No. 225.

duced, owing to the reduction of a portion of the sulphuric acid by the hydrobromic acid which is first evolved, thus—

$$H_2SO_4 + 2HBr = SO_2 + 2H_2O + Br_2.$$

(5.) A dilute aqueous solution of hydrobromic acid may also be obtained by passing a stream of sulphuretted hydrogen through bromine water—

$$H_2S + Br_2 = S + 2HBr.$$

(6.) Hydrobromic acid is readily obtained by the action of bromine upon certain hydrocarbons, such as turpentine or melted paraffin. The action is one of substitution, one atom of bromine replacing one atom of hydrogen in the compound, and the hydrogen so displaced combining with a second bromine atom to form hydrobromic acid. Thus, if the hydrocarbon be represented by the general formula, C_nH_{2n+2}, the action of bromine will be represented thus—

$$C_nH_{2n+2} + Br_2 = C_nH_{2n+1}Br + HBr.$$

Properties.—Hydrobromic acid is a colourless, pungent-smelling gas, which fumes strongly in the air. It is extremely soluble in water, forming an acid liquid strongly resembling aqueous hydrochloric acid.

When boiled, this solution loses either acid or water, until it reaches a degree of concentration at which it contains 48 per cent. of hydrobromic acid. The acid of this strength then continues to boil unchanged at 126°. As with hydrochloric acid, the strength of the liquid which boils at a constant temperature depends upon the pressure.

Hydrobromic acid is decomposed by chlorine, with the liberation of bromine—

$$2HBr + Cl_2 = 2HCl + Br_2.$$

In its chemical behaviour, hydrobromic acid closely resembles hydrochloric acid, and this resemblance is extended to the bromides. All bromides are soluble in water, except mercurous bromide, silver bromide, and lead bromide, the latter being slightly soluble.

OXYACIDS OF BROMINE.

No oxides of bromine corresponding with the oxides of chlorine have as yet been obtained; two oxyacids, however, are known, viz.:—

Hypobromous acid . . .	HbrO.
Bromic acid	$HBrO_3$.

HYPOBROMOUS ACID.

Formula, HBrO.

Mode of Formation.—An aqueous solution of hypobromous acid may be obtained by shaking together a mixture of bromine water and precipitated mercuric oxide, the reaction being analogous to that by which hypochlorous acid is prepared—

$$HgO + H_2O + 2Br_2 = HgBr_2 + 2HBrO.$$

Properties.—Hypobromous acid is an unstable compound; it breaks up on distillation into oxygen and bromine. By heating to 40° in vacuo, however, it can be distilled without decomposition. The aqueous liquid so obtained has a pale-yellow colour. It readily gives up its oxygen, and is a strong bleaching agent; when heated to about 60° it decomposes.

BROMIC ACID.

Formula, $HBrO_3$.

Modes of Formation.—(1.) This acid is only known in aqueous solution; in this form it may be obtained by the action of bromine upon silver bromate in the presence of water—

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

The insoluble silver bromide separates out, and the aqueous acid can be decanted from the precipitate.

(2.) A solution of this acid, mixed with hydrochloric acid, is also formed when chlorine is passed through bromine water—

$$Br_2 + 5Cl_2 + 6H_2O = 10HCl + 2HBrO_3.$$

(3.) The decomposition of barium bromate by the requisite weight of sulphuric acid affords the best method for the preparation of a pure aqueous solution of bromic acid—

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2HBrO_3.$$

Properties.—Bromic acid is an unstable, strongly acid substance, closely resembling chloric acid. The aqueous solution may be concentrated in vacuo until it contains about 50 per cent. of bromic acid, representing a composition of 1 molecule of the acid to 7 of water. Beyond this degree of concentration, or if heated to 100°, the acid decomposes into bromine, oxygen, and water.

The bromates are formed by reactions similar to those by which the chlorates are produced; thus, by adding bromine to a solution of potassium hydroxide, a mixture of potassium bromide and bromate is obtained—

$$6KHO + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

And the two salts can be separated by crystallisation, owing to the greater solubility of the bromide.

The bromates decompose on being heated, some with the liberation of oxygen and formation of bromide—

$$KBrO_3 = KBr + 3O,$$

but without the intermediate production of a perbromate. Others give off their bromine as well as a part of the oxygen they contain, leaving the metal in combination with oxygen—

$$Mg(BrO_3)_2 = MgO + Br_2 + 5O.$$

IODINE.

Symbol, I. Atomic weight=126.97. Molecular weight=253.94.
Vapour density=126.97.

History.—Iodine was discovered by Courtois (1812), who observed that a beautiful violet vapour was evolved during his endeavours to prepare nitre from liquors obtained by lixiviating the ashes of burnt seaweed. The substance was subsequently investigated by Gay-Lussac.

Occurrence.—Like all the other members of this group of elements, iodine is not found in nature in the uncombined condition.* In combination it occurs associated principally with potassium, sodium, magnesium, and calcium, as iodides and iodates.

Iodine is a widely distributed element, although not occurring in more than small quantities in any particular source. Thus it is found in small quantities in sea-water and in both marine plants and animals. The amount of iodine in seaweed varies with different plants; generally speaking, those from greater depths contain more than weeds which grow in comparatively shallow waters.

	Dry Weeds.	Per Cent. of Iodine.
Drift weed	Laminaria digitata (stem)	0.4535
	Laminaria stenophylla	0.4777
Cut weed	Fucus serratus	0.0856
	Ascophyllum nodosum	0.0572

Iodine is also found in small quantities in many mineral waters and medicinal springs.

In small quantities iodine is present in the natural sodium nitrate of Chili and Peru, known as Chili saltpetre, and at the present day this constitutes the most abundant source of this element.

Mode of Formation.—Iodine may be readily obtained by a precisely similar reaction to that by which both bromine and chlorine are produced; thus, if potassium iodide be mixed with manganese dioxide and sulphuric acid, and the mixture gently heated in a retort, iodine distils over and condenses in the form of greyish-black crystals—

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

Manufacturing Processes.—On an industrial scale iodine is obtained from two sources, namely, from seaweed and from caliche (Chili saltpetre).

(1.) *From seaweed.* The weeds chiefly employed are the *Laminaria digitata* and *Laminaria stenophylla*. The weed is burnt in shallow pits, care being taken to avoid too high a temperature; the maximum yield of iodine being obtained if the ash is not allowed to fuse. This ash is technically known as *kelp*, and if the weed is properly burnt, it should yield a kelp containing from 25 to 30 lbs. of iodine per ton. The kelpers, however, usually lose about half

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* It is on record (Wanklyn, *Chem. News*, 54) that a minute quantity of free iodine was found in the water from Woodhall Spa.

the iodine on account of burning the weed at too high a temperature, thereby fusing the ash into a hard slag, instead of obtaining a porous residue.

An improved process of carbonising the weed was introduced by Stanford (1863), in which it was heated in large retorts, whereby the volatile products of the distillation, consisting largely of tar and ammoniacal liquor, could be collected. The kelp obtained by this method is in a very porous condition, and contains the whole of the iodine originally present in the weed.

A still more recent process for extracting the iodine from seaweed, and at the same time obtaining other useful materials, has since been discovered by Stanford. The weed is boiled with sodium carbonate and filtered : the residue consists of a substance called *algulose*. Hydrochloric acid is added to the filtered liquid, which precipitates a compound known as *alginic acid*, and this is again separated by filtration. The liquor is neutralised with sodium hydroxide, evaporated to dryness and carbonised. The residue, which is known as "kelp substitute," contains all the iodine, as well as the potash salts, and should yield about 30 lbs. of iodine per ton.

[The alginic acid obtained in this process is purified and converted into the sodium salt, which constitutes the commercial "algin," a material of a gelatinous or albuminous nature which has lately been put to a number of useful applications.]

The kelp obtained by either of these methods is lixiviated with water in large iron vats, whereby all the soluble salts are extracted. This aqueous liquid is concentrated in large open boiling pans, and the less soluble salts, viz., the alkaline sulphates, carbonates, and chlorides, are allowed to crystallise. The mother-liquor is then mixed with sulphuric acid and allowed to stand. The sulphuric acid decomposes any sulphides and sulphites which may be present, with the separation of sulphur ; it also converts the bromides and iodides into the corresponding sulphates, with the liberation of hydrobromic and hydriodic acids which remain in solution, while the alkaline sulphates are deposited from the liquid, and are technically known as *plate sulphate*. The liquor is then transferred to the *iodine still*, which is an iron pot furnished with a leaden cover into which two exit-pipes are fixed (Fig. 106). These are connected to a series (usually ten in each row) of large earthenware jars or *aludels*. A gentle heat is applied, and manganese dioxide is introduced from time to time through the opening. The iodine is evolved according to the following equation—

$$2HI + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + I_2,$$

and condenses in the jars. These vessels are also furnished with a tubulus upon their under side, so that the water which is evolved during the distillation can drain out, and run off down the trough in which the jars are resting.

(2.) *From Chili saltpetre.* The crude sodium nitrate of Chili and Peru, known as *caliche*, contains small quantities of iodine, chiefly as sodium iodate. Although the amount of iodine in caliche is only very small, averaging about 0.2 per cent., in view of the enormous quantity of nitrate that is turned out, the aggregate amount of iodine is very great. The iodine is now extracted, and the supply of this element that is now manufactured from this source is more than the total consumption of iodine in the whole world. The process is based upon the fact, that when a solution of hydrogen sodium sulphite (sodium bisulphite) is added to a solution of an iodate, iodine is precipitated, thus—

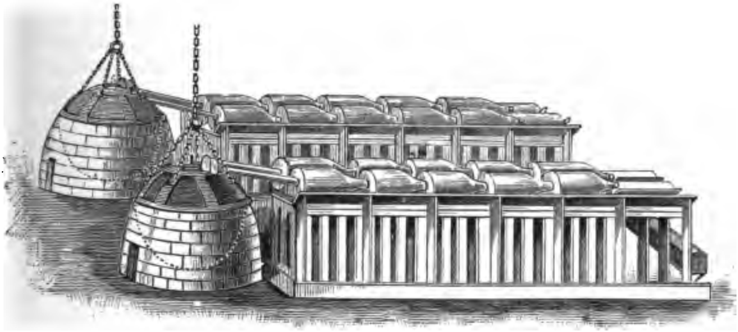

FIG. 106.

$$2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2.$$

The final mother-liquor from the sodium nitrate, or caliche, in which all the iodate has concentrated, contains as much as 22 per cent. of this salt. This liquor is mixed with the requisite proportion of the hydrogen sodium sulphite solution, in large lead-lined vats, and the precipitated iodine allowed to settle. It is then washed and pressed into blocks, and is found to contain from 80 to 85 per cent. of iodine. This impure product is then distilled at a gentle heat from iron retorts, the vapour being condensed in a series of earthenware receivers much as in the older method.

Properties.—Iodine is a bluish-black shining solid, somewhat resembling graphite in lustre and general outward appearance. It crystallises in large brilliant plates, which have a specific gravity of 4.95. When heated to 107° iodine melts and gives off vapour having a beautiful violet colour. Its boiling-point is about 175°.

Iodine vaporises slowly at ordinary temperatures, and sublimes from one part to another of a bottle in which a small quantity of it is contained. The smell of iodine vapour is somewhat irritating and unpleasant, recalling the smell of moderately diluted chlorine. When iodine vapour is heated it passes from a violet colour to a deep indigo blue.* This change in the colour is accompanied by a diminution of the vapour-density. Up to a temperature of 700° the density of iodine corresponds to the formula I_2; as the temperature is raised the density gradually diminishes, until at 1468° it is reduced to less than two-thirds. At this point, 73.1 per cent. of the iodine molecules have become dissociated into single atoms.

Iodine is slightly soluble in water, 1 gramme of iodine being dissolved by 5.524 litres of water at 10°. This dilute solution, however, has a perceptible brown colour. Iodine is freely soluble in aqueous potassium iodide solution, in alcohol, ether, and aqueous hydriodic acid; in all these solvents it dissolves to a dark reddish-brown solution. In chloroform, carbon disulphide, and many liquid hydrocarbons, iodine is also soluble, but in these solvents it dissolves to a deep violet solution resembling the colour of the vapour.

When iodine is brought into contact with starch it forms an intense blue colour. This reaction is so extremely delicate that it is capable of revealing the minutest trace of iodine. The exact nature of this blue compound is not known. The colour disappears when the liquid is heated to about 80°, but returns on cooling; continued boiling destroys it permanently.

In its chemical relations iodine resembles chlorine and bromine, but with a lesser degree of energy. Both these elements are

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* "Chemical Lecture Experiments," new ed., No. 231.

capable of displacing iodine from its combinations with electropositive elements, thus—

$$KI + Br = KBr + I.$$
$$KI + Cl = KCl + I.$$

Iodine combines with many elements, both metals and non-metals, forming iodides. Phosphorus, when brought in contact with iodine, at once melts and inflames ; antimony powder dropped into iodine vapour also spontaneously inflames. When mercury and iodine are gently heated, energetic combination takes place, and mercuric iodide is formed.

HYDRIODIC ACID (*Hydrogen Iodide*).

Formula HI. Molecular weight = 127.98. Density = 63.99.

Modes of Formation.—(1.) Hydriodic acid can be obtained synthetically by passing a mixture of hydrogen and iodine vapour over strongly heated, finely divided platinum.

FIG. 107.

(2.) It is also obtained by the action of phosphoric acid upon sodium or potassium iodide (see Hydrobromic Acid).

As in the case of the corresponding bromine compound, sulphuric acid cannot be employed, as by its action upon the iodide, iodine and sulphur dioxide are liberated, thus—

$$2KI + 3H_2SO_4 = 2HKSO_4 + 2H_2O + SO_2 + I_2.$$

(3.) Hydriodic acid is produced by the action of sulphuretted hydrogen upon iodine (p. 410). At the ordinary temperature, and in the absence of water, these two substances do not react, hydriodic acid being an endothermic compound (p. 168); but if the iodine be suspended in water and sulphuretted hydrogen passed through, the heat of solution of the hydriodic acid supplies the necessary energy to enable the action to proceed. When, however, the solution reaches a sp. gr. of 1.56 the action ceases, because, as Naumann has shown, the heat produced by the solution of the product is insufficient to carry on the process beyond this degree of concentration.

(4.) Hydriodic acid is most readily prepared by the action of phosphorus upon iodine in the presence of water—

$$P + 5I + 4H_2O = H_3PO_4 + 5HI.$$

The red phosphorus and iodine for this reaction may be placed in a dry flask, and water gradually dropped upon the mixture, when hydriodic acid is rapidly evolved. The gas is allowed to pass through a U-tube containing red phosphorus, in order to arrest any iodine vapour which may accompany it. Hydriodic acid may be collected over mercury or by displacement, as shown in Fig. 107.

Properties.—Hydriodic acid is a colourless, pungent-smelling gas, which fumes strongly on coming into the air. The gas is readily decomposed by heat into hydrogen and iodine. Thus, if a heated wire be thrust into the gas, or if a spiral of platinum wire be heated in the gas by means of an electric current, the violet vapour of iodine at once makes its appearance.

When mixed with chlorine, hydriodic acid is at once decomposed, with the liberation of iodine, thus—

$$2HI + Cl_2 = 2HCl + I_2.$$

Hydriodic acid is one of the most readily liquefied gases; at 0°, and under a pressure of four atmospheres, it condenses to a colourless liquid.

The gas is extremely soluble in water. An aqueous solution of it is readily produced by allowing the gas, obtained by the method of preparation above described, to pass into water. In order to prevent the water from being drawn back into the generating flask, it is convenient to pass the gas through a retort arranged in the position seen in Fig. 108. Should there be any back rush of water, owing to the intermission of the evolution of gas in the apparatus, the liquid in the beaker will be drawn up into the retort and there lodge, leaving the end of the neck open to the air.

FIG. 108.

A saturated aqueous solution of hydriodic acid at 0° has a specific gravity of 2. At the ordinary pressure the strongest acid that can be obtained by distillation has a specific gravity of 1.67, and contains 57.7 per cent. of hydriodic acid. This solution boils at 127°. As in the case of the corresponding bromine and chlorine compounds, the particular strength of acid which has a constant boiling-point is a function of the pressure.

Aqueous hydriodic acid, when freshly prepared, is colourless, but it rapidly turns brown, owing to the oxidation of the compound and the solution of the liberated iodine in the acid—

$$4HI + O_2 = 2H_2O + 2I_2.$$

OXIDE AND OXYACIDS OF IODINE.

One compound of iodine with oxygen is known, and three oxyacids, viz. :—

Iodine pentoxide	I_2O_5.
Iodic acid	HIO_3
Periodic acid	HIO_4.
Hypoiodous acid . . .	HIO.

IODINE PENTOXIDE (*Iodic Anhydride*).

Formula, I_2O_5.

Mode of Formation.—When iodic acid is heated to 170°, it loses water and is converted into the pentoxide—

$$2HIO_3 = H_2O + I_2O_5.$$

Properties.—Iodine pentoxide is a white crystalline solid body. It is soluble in water, combining with a molecule of the water to form iodic acid. Iodine pentoxide is more stable than any of the oxides of the other halogens, but, when heated to a temperature of 300°, it decomposes into its elements.

IODIC ACID.

Formula, HIO_3.

Modes of Formation.—(1.) Iodic acid can be prepared by adding to a solution of barium iodate the requisite amount of sulphuric acid demanded by the equation—

$$Ba(IO_3)_2 + H_2SO_4 = BaSO_4 + 2HIO_3.$$

The aqueous solution of iodic acid is decanted from the precipitated barium sulphate, and may be concentrated at 100° without being decomposed.

(2.) When chlorine is passed through water in which powdered iodine is suspended, a mixture of iodic acid and hydrochloric acid is produced—

$$3H_2O + I + 5Cl = 5HCl + HIO_3.$$

The hydrochloric acid may be removed by the addition of precipitated silver oxide to the solution, and separating the precipitated silver chloride by filtration.

(3.) Iodic acid is most conveniently prepared by heating iodine with nitric acid, whereby the iodine is oxidised and a mixture of oxides of nitrogen is evolved as dense red vapours—

$$3HNO_3 + I = HIO_3 + H_2O + NO + 2NO_2.$$

Properties.—Iodic acid is a white crystalline solid, soluble in water. The aqueous solution shows an acid reaction with litmus, but the colour is ultimately discharged by the bleaching action of the compound. Iodic acid does not form any blue colour with starch; being, however, an oxidising substance, it readily gives up oxygen to such reducing agents as sulphur dioxide, sulphuretted hydrogen, or hydriodic acid, with the liberation of iodine, thus—

$$2HIO_3 + 4H_2O + 5SO_2 = 5H_2SO_4 + I_2.$$
$$2HIO_3 + 5H_2S = 5S + 6H_2O + I_2.$$
$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

If, therefore, a small quantity of sulphurous acid be added to a dilute solution of iodic acid, previously mixed with starch, the blue iodide of starch will be formed. This reaction affords an excellent illustration of the time required for certain chemical changes to go forward. It is readily possible to obtain an interval of 30 to 60 seconds between the addition of the sulphurous acid and appearance of any visible result, when at the expiration of that time the whole mass of the liquid suddenly turns blue.*

Iodates.—When iodine is dissolved in potassium hydroxide, a mixture of potassium iodide and iodate is produced by an analogous reaction to that which takes place with either bromine or chlorine—

$$6KHO+3I_2=5KI+KIO_3+3H_2O.$$

With the exception of the iodates of the alkali metals, the iodates are for the most part insoluble in water. On being heated they behave in a similar manner to the bromates, some being decomposed into an iodide and oxygen, while others leave a metallic oxide and evolve iodine as well as oxygen. The alkaline iodates are capable of uniting with iodic acid, forming salts which are termed *acid* and *di-acid* iodates, thus—

Normal potassium iodate . . .	KIO_3.
Acid potassium iodate . . .	KIO_3,HIO_3.
Di-acid potassium iodate . . .	$KIO_3,2HIO_3$.

PERIODIC ACID.

Formula, $HIO_4,2H_2O$ or H_5IO_6.

Modes of Formation.—(1.) The compound represented by the formula HIO_4 has never been obtained; when aqueous solutions of periodic acid are evaporated, the compound which crystallises out has the composition $HIO_4,2H_2O$, or H_5IO_6.

It may be obtained by boiling silver periodate with water, when an insoluble basic silver salt is produced—

$$2AgIO_4+4H_2O=Ag_2H_3IO_6+HIO_4,2H_2O.$$

The silver periodate is prepared by passing chlorine into an aqueous solu-

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* See Experiment 246, "Chemical Lecture Experiments," new ed.

tion of sodium iodate and sodium hydroxide, when the sparingly soluble disodium periodate separates out—

$$NaIO_3+3NaHO+Cl_2=2NaCl+Na_2H_3IO_6.$$

This sodium salt is then dissolved in nitric acid and silver nitrate added, whereby $AgIO_4$ is formed, which crystallises out on concentration—

$$\left\{\begin{array}{l} 2Na_2H_3IO_6+2HNO_3=2NaNO_3+4H_2O+2NaIO_4. \\ 2NaIO_4+2AgNO_3=2NaNO_3+2AgIO_4. \end{array}\right.$$

(2.) Periodic acid is also formed by the addition of iodine to an aqueous solution of perchloric acid—

$$2HClO_4+2H_2O+I_2=Cl_2+2HIO_4,2H_2O.$$

Properties.—The acid having the composition $HIO_4,2H_2O$ is a colourless, crystalline, deliquescent substance. It melts at 133°, and at 150° is decomposed into iodine pentoxide, water, and oxygen—

$$2H_5IO_6=I_2O_5+5H_2O+O_2.$$

The acid cannot be converted into HIO_4 by heat, for oxygen is evolved as soon as water begins to be given off.

The Periodates constitute a numerous class of salts, many of them being of a highly complex composition. On the assumption that iodine is monovalent in these compounds, their classification is somewhat difficult, and they must be represented as associations of molecules of salts of the unknown monobasic periodic acid, HIO_4, with metallic oxide and water in various proportions—thus, the silver periodate in the foregoing equation, $Ag_2H_3IO_6$, would be expressed by the formula, $2AgIO_4,Ag_2O,2H_2O$.

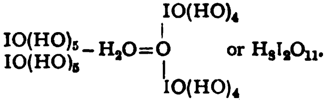
The classification of these compounds is much simplified if we regard iodine as here functioning as a heptavalent element. On this assumption the periodates may be considered as the salts of various hypothetical acids, which are all derived from the compound $I(HO)_7$ (itself hypothetical) by the withdrawal of varying quantities of water. Thus, by the successive removal of one molecule of water, the following three acids would be formed—

$I(HO)_7 - H_2O = IO(HO)_5$ . . . H_5IO_6. (1.)
$IO(HO)_5 - H_2O = IO_2(HO)_3$ . . . H_3IO_5. (2.)
$IO_2(HO)_3 - H_2O = IO_3(HO)$ . . . HIO_4. (3.)

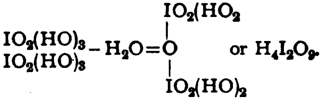
From these three acids the following salts may be regarded as being derived—

(1.) $Na_2H_3IO_6$; $Ag_2H_3IO_6$; Ag_5IO_6; $Ba_5(IO_6)_2$.
(2.) Ag_3IO_5; $Pb_3(IO_5)_2$.
(3.) KIO_4; $AgIO_4$.

By the abstraction of one molecule of water from *two* molecules of these acids, still more complex acids would be derived, thus—



$$\begin{array}{l} IO(HO)_5 \\ IO(HO)_5 \end{array} - H_2O = \begin{array}{c} IO(HO)_4 \\ | \\ O \\ | \\ IO(HO)_4 \end{array} \quad \text{or } H_8I_2O_{11}. \qquad (4.)$$



$$\begin{array}{l} IO_2(HO)_3 \\ IO_2(HO)_3 \end{array} - H_2O = \begin{array}{c} IO_2(HO_2 \\ | \\ O \\ | \\ IO_2(HO)_2 \end{array} \quad \text{or } H_4I_2O_9. \qquad (5.)$$

And from these two acids the following periodates may be regarded as being derived—

(4.) $Zn_4I_2O_{11}$; $Ba_4I_2O_{11}$.
(5.) $Ag_4I_2O_9$; $Ca_2I_2O_9$; $Ba_2I_2O_9$.

HYPOIODOUS ACID AND HYPOIODITES.

When an aqueous solution of iodine is added to either ammonia, potassium, or sodium hydroxides, lime-water or baryta-water, a colourless solution is obtained which possesses bleaching properties. The liquid is a dilute solution of the hypoiodite and iodide of the alkali used. Somewhat stronger solutions may be produced by adding small quantities of powdered iodine to the mixture—

$$2KHO + I_2 + Aq = KIO + KI + H_2O + Aq.$$

A dilute solution of the acid itself is obtained by shaking mercuric oxide with iodine and water (see Hypochlorous Acid, p. 373).

The solution of the alkaline hypoiodite obtained by the above reaction possesses well-marked bleaching properties. When freshly prepared it is without action upon starch, but is immediately decomposed by even so feeble an acid as carbonic acid, when the blue starch compound is at once formed.

A compound of iodine with lime, analogous to *bleaching powder*, has been obtained by shaking powdered iodine with milk of lime. The compound in the presence of water appears to behave in the same way as bleaching powder, yielding a solution of calcium hypoiodite and calcium iodide—

$$2Ca(OI)I = Ca(OI)_2 + CaI_2.$$

On filtering the mixture a colourless liquid is obtained, which gives no reaction with starch, but which yields iodine when treated with an acid.

Neither the acid nor any of its salts has been isolated, being known only in dilute solution. The compounds are all extremely unstable, decomposing at the ordinary temperature in a few hours, and in a few minutes when the solutions are boiled; the salts passing into iodides and iodates—

$$3KIO = 2KI + KIO_3,$$

while the acid decomposes first into hydriodic and iodic acids, which then react upon each other with elimination of free iodine.

COMPOUNDS OF THE HALOGENS WITH EACH OTHER.

Chlorine unites both with bromine and with iodine, and the two latter elements combine with each other.

(1.) **Chlorine and Bromine.**—*Bromine monochloride.* This substance is obtained as a reddish-yellow liquid, when chlorine gas is passed into bromine. The compound is believed to have the composition BrCl.

(2.) **Chlorine and Iodine.**—*Iodine monochloride,* ICl. When dry chlorine is passed over iodine, the latter rapidly melts, forming a dark reddish-brown liquid, strongly resembling bromine in appearance. The liquid solidifies to a mass of red prismatic crystals, which melt at 25°. It is decomposed by water into iodic and hydrochloric acids, and iodine is liberated—

$$5ICl+3H_2O=HIO_3+5HCl+2I_2.$$

Iodine trichloride, ICl_3. This compound is formed by passing an excess of chlorine over iodine, or by passing chlorine through iodine monochloride. It is also formed when hydriodic acid is acted upon by an excess of chlorine—

$$HI+2Cl_2=HCl+ICl_3.$$

Iodine trichloride is a yellow solid substance, crystallising in long brilliant needle-shaped crystals, which sublime at the ordinary temperature. When gently warmed it melts, at the same time dissociating into chlorine and the monochloride; on cooling, reunion takes place with the reformation of ICl_3.

(3.) **Bromine and Iodine.**—Two compounds of these elements are believed to exist, viz., a crystalline solid and a deep-coloured liquid. Their composition is probably expressed by the formulæ, IBr and IBr_3.

CHAPTER II

THE ELEMENTS OF GROUP VI. (FAMILY B.)

Oxygen, O	16.00	Selenium, Se	79.1
Sulphur, S	32.06	Tellurium, Te	127.6

THE relation in which oxygen, the typical element, stands to the remaining members of the family is very similar to that between fluorine and the other halogens.

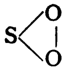
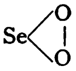
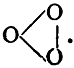
All the elements of this family unite with hydrogen, forming compounds of the type RH_2—

$$OH_2,\quad SH_2,\quad SeH_2,\quad TeH_2\,;$$

but the hydride of oxygen stands apart from the others in many of its attributes. Thus at ordinary temperatures it is a colourless and odourless liquid, while the remaining compounds are all fœtid-smelling and poisonous gases.

Sulphur, selenium, and tellurium each combines with oxygen, forming respectively SO_3, SeO_3, and TeO_3, while none of these elements in a divalent capacity forms a similar compound ; that is to say, no such combinations are known as OS_3, or OSe_3, although amongst themselves they unite, forming SeS_2 and TeS_2.

Sulphur, selenium, and tellurium also unite with oxygen, forming dioxides, SO_2, SeO_2, and TeO_2, in which these elements are possibly tetravalent, in which case the constitution of the compounds will be represented thus, $O=S=O$; $O=Se=O$.

We may, however, consider them as functioning in a divalent capacity, and regard the oxides as constituted thus,  ; , in which case we may look upon ozone as being the corresponding oxygen compound, OO_2, .

All the elements of this family combine with chlorine, producing compounds having the following composition :—

Oxygen.	Sulphur.	Selenium.	Tellurium.
O_2Cl	—	—	—
—	S_2Cl_2	Se_2Cl_2	—
OCl_2	SCl_2	—	$TeCl_2$
—	SCl_4	$SeCl_4$	$TeCl_4$

Oxygen again differs from the other members by alone forming a compound of the type, R_2Cl. This element also shows no tendency to function with a higher atomicity than that of a divalent; while the others unite with four atoms of the halogen, thereby exhibiting their tetravalent nature.

The members of this family pass by a regular gradation from the strongly electro-negative, gaseous, non-metal oxygen to the feebly negative and slightly basic element tellurium, which possesses many of the properties of a true metal. Selenium and tellurium are both elements which lie very close to that ill-defined boundary between the metals and non-metals, and are on this account sometimes termed *metalloids*. In tellurous oxide, TeO_2, we have a compound which is both an acid-forming and a salt-forming oxide, its acidic and basic properties being nearly equally balanced. Thus, it unites with water, forming tellurous acid, H_2TeO_3, corresponding to sulphurous acid, H_2SO_3; while tellurium replaces hydrogen in sulphuric acid, forming tellurium sulphate, $Te(SO_4)_2$.

Of the four elements of this family, oxygen is by far the most abundant, both in combination and in the free state; sulphur is more plentiful than the other two, and tellurium occurs in the smallest quantity.

The element oxygen has already been treated in Part II.

SULPHUR.

Symbol, S. Atomic weight = 32.06. Molecular weight = 64.12.

Occurrence.—In the free state this element occurs chiefly in volcanic districts. In Italy and Sicily large quantities of *native sulphur* are found, which have long been the most important European sources of this substance. Large deposits are to be met with in Transylvania and in Iceland, and it also occurs in beds, often of great thickness, in parts of China, India, California, and the Yellowstone district of the Rocky Mountains. These natural deposits are sometimes found stratified with beds of clay or rock, but they often occur as what are known as "living" beds, in which the sulphur is continuously being formed as the result of chemical decompositions which are at present at work. Such a "living" sulphur bed is known as a *solfatara*, and, as in the case of the Iceland deposits, they are usually found associated with geysers, fumaroles, and other signs of volcanic action.

In combination with hydrogen, sulphur occurs as sulphuretted hydrogen. Enormous quantities of sulphur are found combined with various metals, constituting the important class of substances known as sulphides; as, for example, *galena*, or lead sulphide, PbS; *zinc blende*, or zinc sulphide, ZnS; *pyrites*, or iron sulphide, FeS_2; *copper pyrites*, or copper iron sulphide, $Cu_2Fe_2S_4$; *stibnite*, or antimony sulphide, Sb_2S_3; *cinnabar*, or mercury sulphide, HgS.

In combination with metals and oxygen, sulphur occurs in sulphates, such as *gypsum*, $CaSO_4,2H_2O$; *heavy spar*, $BaSO_4$; *kieserite*, $MgSO_4,H_2O$.

Modes of Formation.—(1.) Sulphur is formed when sulphuretted hydrogen is brought in contact with sulphur dioxide; the two gases mutually decompose one another with the formation of water and the precipitation of sulphur—

$$2H_2S+SO_2=2H_2O+3S.$$

(2.) It is also produced when sulphuretted hydrogen is burnt with an insufficient supply of air—

$$H_2S+O=H_2O+S.$$

This reaction probably takes place in two stages, a portion of the sulphuretted hydrogen burning to sulphur dioxide, and this then reacting upon a further quantity of sulphuretted hydrogen, thus—

$$(a)\ H_2S+3O=H_2O+SO_2.$$
$$(b)\ 2H_2S+SO_2=2H_2O+3S.$$

It is supposed that some of the free sulphur found in volcanic regions has been produced by this action of these two gases upon one another.

Extraction of Sulphur from Native Sulphur.—Natural sulphur is always more or less mixed with earthy or mineral matters, from which it is necessary to free it. This is usually effected by melting the sulphur and allowing it to flow away from the accompanying impurities. The crude sulphur rock is stacked in brick kilns having a sloping floor, and the mass ignited by introducing through openings in the heap burning faggots of brushwood. The heat produced by the combustion of a part of the sulphur causes the remainder to melt and collect upon the sloping floor of the kiln, from which it can be drawn off into rough moulds. The loss of sulphur by this method is very considerable, usually not more than two-thirds of the total amount contained in the rock being obtained.

(3.) Sulphur may be obtained by heating certain metallic sulphides; thus when iron pyrites is heated it yields one-third of its sulphur—

$$3FeS_2 = Fe_3S_4 + S_2.$$

If the pyrites be roasted in kilns, the whole of the sulphur is obtained, partly as free sulphur and partly as sulphur dioxide—

$$3FeS_2 + 5O_2 = Fe_3O_4 + 3SO_2 + 3S.$$

This method was at one time rather extensively employed for the preparation of sulphur on a manufacturing scale, but has now practically gone out of use, the pyrites being usually roasted with excess of air, whereby the whole of the sulphur is converted into sulphur dioxide for use in the manufacture of sulphuric acid.

By a similar process, sulphur is obtained as a bye-product during the roasting of copper pyrites in the first stage of the operation of copper-smelting.

(4.) Large quantities of sulphur are now extracted from the *vat-waste* or *alkali-waste*, obtained in the manufacture of sodium carbonate by the Leblanc process. This material consists largely of an insoluble oxy-sulphide of lime, a compound containing calcium sulphide (CaS) and calcium oxide (CaO) in varying proportions. *Mond's process*, which, however, has now been entirely superseded by *Chance's process* (p. 411), is the following: A current of air is blown through the compound, whereby the calcium sulphide it contains is ultimately converted into a mixture of calcium hydrosulphide (CaH_2S_2), thiosulphate (CaS_2O_3), and polysulphide (CaS_5), according to the following equations—

$$(1.)\ 2CaS + 2H_2O = CaH_2S_2 + CaH_2O_2.$$

This reaction goes forward in several stages, in the course of which a quantity of sulphur is set free; this is then acted upon by the calcium hydroxide, with the formation of calcium polysulphide and calcium thiosulphate, thus—

(2.) $3CaH_2O_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O.$

The materials are alternately oxidised and lixiviated several times, and the liquor is then treated with excess of hydrochloric acid at a temperature of about 60°, which decomposes the various sulphur compounds according to the following equations—

(*a.*) $CaH_2S_2 + 2HCl = CaCl_2 + 2H_2S.$
(*b.*) $CaS_5 + 2HCl = CaCl_2 + H_2S + 4S.$
(*c.*) $CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O.$

The best results are obtained when the sulphur compounds are present in such proportions that the SO_2 evolved by reaction *c* is sufficient to decompose the whole of the SH_2 produced by the other two reactions, so that neither gas escapes—

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

(5.) Sulphur is also obtained from the spent oxide of iron which has been used in the "purifiers" employed upon gas-works. Coal gas contains considerable quantities of sulphuretted hydrogen, which are removed from the gas by passing it through hydrated ferric oxide ($Fe_2H_6O_6$), which absorbs the whole of the sulphuretted hydrogen, thus—

$$Fe_2H_6O_6 + 3H_2S = 2FeS + S + 6H_2O.$$

When the compound has lost its power to absorb sulphuretted hydrogen, the material is thrown out of the purifiers and exposed to air and moisture, when the iron becomes reconverted into the hydrated oxide, and the sulphur is set free—

$$2FeS + 3O + 3H_2O = Fe_2H_6O_6 + 2S.$$

This *revivified* material is then employed for the purification of a further quantity of gas. It is found that after a certain number of revivifying operations the substance begins to lose its power of absorbing any additional sulphuretted hydrogen, and as it then contains nearly half its weight of sulphur, it becomes a valuable source of this element. The sulphur is obtained from it by distillation, or the material may be roasted in special kilns, whereby the sulphur is converted into sulphur dioxide, and employed for the manufacture of sulphuric acid.

Purification.—The crude sulphur obtained by the foregoing methods is purified by distillation, the process being carried out in the arrangement shown in Fig. 109. The sulphur is first melted in an iron pot *d*, and the liquid substance drawn off at will by

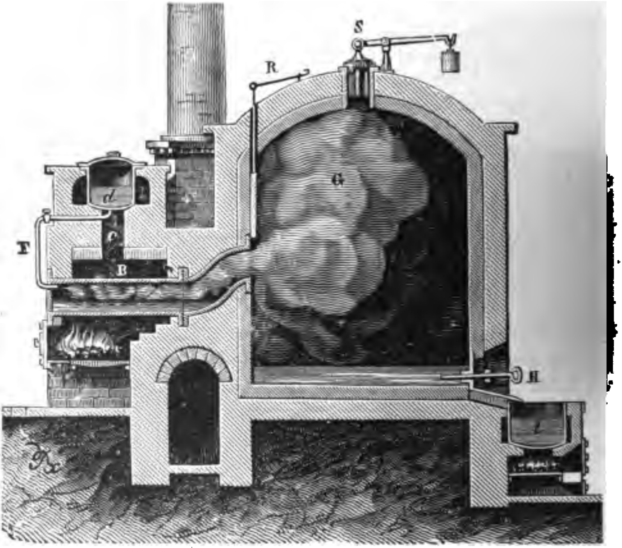


FIG. 109.

means of the pipe F into the retort B. The sulphur is there boiled by means of the fire, and the vapour allowed to issue into the large brickwork chamber G. As the vapour enters the chamber, it condenses upon the walls and floor in the form of a light, powdery deposit, consisting of minute crystals, and constituting the *flowers of sulphur* of commerce. As the process continues, and the brickwork becomes hot, this soft powder melts and collects upon the floor as an amber-coloured liquid, which is run out from time to time from the opening at H, and cast either into large blocks or into cylindrical rods, by means of wooden moulds. In the latter form it is known as *roll sulphur.*

When the sulphur vapour first enters the chamber and mixes with the air, the mixture frequently ignites with a feeble explosion; the chamber, therefore, is furnished with a valve, S, at the top, whereby the pressure developed at the moment of combustion may be relieved.

Properties.—Sulphur, as ordinarily seen, is a pale-yellow brittle crystalline solid. It is insoluble in water, but readily dissolves in carbon disulphide, and to a greater or less degree in turpentine, benzene, chloroform, sulphur chloride, and many other solvents. It is a non-conductor of electricity, and an extremely bad conductor of heat. A piece of sulphur on being very gently warmed, even by being grasped in the hand, may be heard to crack by the unequal heating, and will ultimately fall to pieces. At a temperature of 114.5° sulphur melts to a clear amber-coloured and moderately mobile liquid; on raising the temperature of this liquid its colour rapidly darkens, and at the same time it loses its mobility, until at a temperature of about 230° the mass appears almost black, and is so viscous that it can no longer be poured from the vessel. As the temperature is still further raised, the substance, while retaining its dark colour, again becomes liquid, although it does not regain its original limpidity. At 448° the liquid boils, and is converted into a pale yellowish-brown coloured vapour. On allowing the boiling sulphur to cool, it passes through the same changes in reverse order until it solidifies.

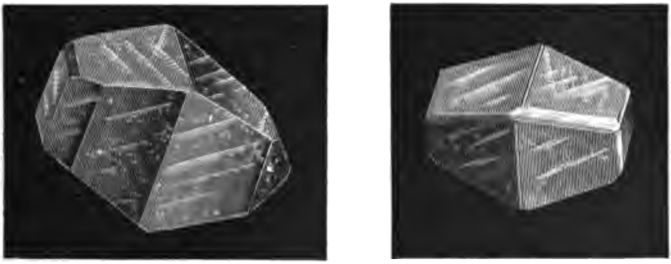


FIG. 110.

When the vapour of sulphur is heated to 1000°, it is converted into a true gas, and has a density of 32, one litre of the gas weighing 32 criths.

Sulphur is known to exist in four allotropic modifications, two of which are crystalline and two amorphous.

(α) "*Rhombic*" *Sulphur.*—Of the two crystalline varieties this is the more stable. Sulphur, therefore, that occurs native is found crystallised in this form, namely, orthorhombic pyramids. It may be obtained by allowing a solution of sulphur in carbon disulphide to slowly evaporate. Fig. 110 represents two large crystals of sulphur obtained in this way.

Orthorhombic crystals of sulphur can also be obtained under certain conditions when melted sulphur is allowed to crystallise. Sulphur in the liquid condition exhibits the phenomenon of suspended solidification to a very high degree, and if the liquid be carefully cooled out of contact with air, the temperature may fall to 90° before solidification takes place. If into the liquid in this state a crystal of the rhombic variety be dropped, the sulphur begins to solidify in crystals of that form. If the superfused sulphur be contained in a hermetically closed flask, the liquid frequently deposits orthorhombic crystals, and by allowing the mass to partially solidify, and quickly inverting the flask, the crystals may be seen upon the bottom of the vessel.

FIG. 111.

The specific gravity of this form of sulphur is 2.05.

(β) "*Prismatic*" *Sulphur.*—When melted sulphur is allowed to cool under ordinary conditions, such as in a crucible or beaker, it crystallises in the form of prismatic needles, belonging to the monoclinic or monosymmetric system. By allowing the mass to partially solidify, and pouring off the still liquid portion, these crystals will be seen lining the inside of the beaker as long translucent prisms. Fig. 111 shows such a mass of crystals. Prismatic crystals of sulphur are also obtained when this element is crystallised from a hot solution in oil of turpentine.

The specific gravity of this form of sulphur is less than that of the orthorhombic variety, being 1.98.

At ordinary temperatures this modification is unstable, and in the course of a day or two the crystals lose their translucent appearance, owing to their becoming broken down into a number of smaller crystals of the rhombic variety, and present the opaque yellow appearance of ordinary roll sulphur. This change from the prismatic to the "rhombic" variety, which takes place more quickly when the crystals are scratched or subjected to vibration, is attended with evolution of heat. When monoclinic sulphur is thrown into carbon disulphide, its transformation into the stable modification takes place rapidly, and in this way, by means of a thermopile, the heat evolved by the change may be rendered evident. As carbon disulphide, however, at once exerts its solvent action upon the "rhombic" sulphur the moment it is formed, the reduction of temperature resulting from this cause would completely overbalance and mask the more feeble heat effect produced by the passage of the sulphur from the unstable to the stable form. In order, therefore, to render evident the heat resulting from the change of crystalline form, the carbon disulphide must be previously allowed to dissolve as much sulphur as it can take up. If a small quantity of carbon disulphide, so saturated with sulphur, be placed in a corked flask, and stood upon the face of a thermo-electric pile* in connection with a galvanometer, and a quantity of prismatic crystals of sulphur be quickly thrown into the liquid, a sensible deflection of the galvanometer needle will be seen in the direction caused by heat.

Although under ordinary conditions monoclinic sulphur is unstable and passes into the "rhombic" form, at temperatures between

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* The thermo-electric pile is a delicate physical instrument employed for registering slight changes of temperature; for descriptions of the apparatus the student must consult text-books on physics.

100° and 114° it appears to be the more stable variety, for at this temperature "rhombic" sulphur passes into the monoclinic variety.

(γ) *Plastic Sulphur.*—When sulphur which has been heated until it reaches the viscous condition is suddenly plunged into water, or when boiling sulphur is poured in a thin stream into water, the substance solidifies to a tough elastic material somewhat resembling indiarubber. The sulphur in this form is known as *plastic sulphur.* This variety is best obtained by distilling a quantity of ordinary sulphur from a glass retort (Fig. 112), and allowing the distilled liquid to flow in a fine stream into cold water placed for its reception. As the liquid sulphur falls into the water, it congeals to the plastic condition as a continuous thread, which winds itself in a regular manner into beautiful coils of a delicate translucent amber colour. The specific gravity of plastic sulphur is 1.95, and it is not soluble in carbon disulphide. At ordinary temperatures this allotrope of sulphur is gradually transformed into the stable "rhombic" variety; in the course of a few days it loses its transparency and elasticity, and becomes converted into the ordinary lemon-yellow brittle condition of common sulphur. This change takes place more quickly if the plastic material be stretched and worked between the fingers, and still more readily by heating it for a few moments to 100°, and allowing it again to cool.

FIG. 112.

(δ) *White Amorphous Sulphur.*—When sulphur is heated, and the vapour condensed upon a cool surface, as in the formation of ordinary flowers of sulphur, although the greater portion of the sulphur is sublimed in the orthorhombic form, the sublimate contains a small amount of sulphur in the form of an amorphous powder, which is almost milk-white in colour.

This modification is best obtained by treating flowers of sulphur, which usually contains as much as 5 or 6 per cent. of amorphous sulphur, with carbon disulphide, whereby the orthorhombic variety is dissolved, and the white amorphous substance, which is insoluble in that liquid, is left behind. By filtering the liquid and washing the residue with carbon disulphide until the whole of the soluble sulphur is removed, the amorphous powder may be obtained in a state of purity.

This amorphous substance is also produced in small quantity, by the action of light upon a solution of sulphur in carbon disulphide. Thus, if a perfectly clear solution of sulphur in this liquid be placed for even a few minutes in the path of a beam of electric light, the solution will be seen to become rapidly turbid, owing to the formation of this insoluble modification.

This milk-white amorphous modification is stable at the ordinary temperature, and therefore does not pass spontaneously into the rhombic variety. When heated to a temperature of 100°, it quickly becomes yellow in colour, and is then readily soluble in carbon disulphide, having been transformed at that temperature into the ordinary stable form.

Milk of Sulphur.—This substance is a medicinal preparation, obtained by precipitating sulphur from a polysulphide of lime by means of hydrochloric acid. Flowers of sulphur and milk of lime are boiled together for some time, and after settling the clear reddish liquid containing the calcium polysulphides is decanted off, and hydrochloric acid added to it; calcium chloride is formed, and sulphur in a fine state of subdivision is precipitated—

$$CaS_x + 2HCl = CaCl_2 + H_2S + (x-1)S.$$

The product so obtained is pale yellow in colour, and consists of ordinary sulphur often contaminated with considerable quantities of calcium sulphate, derived from sulphuric acid present in the hydrochloric acid employed in the precipitation.

When sulphur in any of its modifications is heated in the air, it takes fire and burns with a pale blue flame, giving rise to sulphur dioxide; when burnt in oxygen a small quantity of sulphur trioxide is at the same time produced.

Finely divided sulphur, when exposed to air and moisture, undergoes slow oxidation even at ordinary temperatures, with the formation of sulphuric acid. Thus, if flowers of sulphur be moistened with water and freely exposed to the air, in a short time the water will be distinctly acid. On this account sulphur that is used for pyrotechnic purposes is thoroughly washed and dried, and preserved in warm dry places.

Sulphur combines directly with many metals under the influence of heat, forming sulphides, the union in many cases being accompanied by vivid combustion. Thus, a strip of copper, when introduced into sulphur vapour, burns brilliantly with the formation of copper sulphide, and a red-hot bar of iron, when pressed against a roll of sulphur, burns in the vapour which is generated, and the molten sulphide falls in scintillating masses through the air—

$$Fe + S = FeS.$$

Heated with sodium or potassium, the alkaline sulphides are formed with deflagration—

$$K_2 + S = K_2S.$$

COMPOUNDS OF SULPHUR WITH HYDROGEN.

Two compounds of these elements are known, namely—

Hydrogen sulphide or sulphuretted hydrogen	H_2S.
Hydrogen persulphide	H_2S_2.

HYDROGEN SULPHIDE.

Formula, H_2S. Molecular weight = 34.08. Density = 17.04.

Occurrence.—This gas is evolved in volcanic regions, and is met with in solution in sulphur mineral waters.

Modes of Formation.—(1.) Sulphuretted hydrogen may be formed by the direct union of its elements, by passing a mixture of hydrogen and the vapour of sulphur through a strongly heated tube. In small quantity it is produced when hydrogen is passed into boiling sulphur, or over certain heated metallic sulphides.

(2.) Sulphuretted hydrogen is most readily obtained by the action of either hydrochloric or sulphuric acid upon ferrous sulphide, thus—

$$FeS + 2HCl = FeCl_2 + H_2S.$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The ferrous sulphide in broken fragments is placed in a two-necked bottle, similar to the apparatus (Fig. 29) employed for the preparation of hydrogen, and the dilute acid poured upon it. The gas is rapidly evolved without the application of heat. The gas obtained by this method always contains free hydrogen, owing to the presence of uncombined iron in the ferrous sulphide.

(3.) Pure sulphuretted hydrogen may be obtained by heating antimony trisulphide (grey antimony ore) with strong hydrochloric acid, when antimony trichloride is produced and hydrogen sulphide evolved—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

(4.) Sulphuretted hydrogen is produced during the putrefaction of organic substances containing sulphur, the offensive smell of a decomposing egg being due to the presence of this gas. It is also produced during the destructive distillation of coal, by the direct union of hydrogen with the sulphur contained in the pyrites, hence coal gas always contains sulphuretted hydrogen amongst its impurities.

Properties.—Sulphuretted hydrogen is a colourless gas, having a somewhat sickly sweetish taste and an extremely offensive odour. It acts as a powerful poison when inhaled in the pure state, and even when very largely diluted with air it gives rise to dizziness and headache. Its poisonous effects are more marked upon some animals than others : thus, a bird was found to die in an atmosphere containing only $\frac{1}{1500}$ of sulphuretted hydrogen, while it required an amount equal to $\frac{1}{200}$ to poison a hare ; and again, cold-blooded animals are in no way affected by inhaling these proportions of the gas. Sulphuretted hydrogen is moderately soluble in water ; at ordinary temperatures water dissolves about three times its own volume of the gas. In collecting it over water, therefore, considerable loss results unless the water be warm. The coefficient of absorption by water at 0° is 4.3706.

The aqueous solution gives an acid reaction with litmus, and possesses the taste and smell of the gas. It quickly decomposes on exposure to air, the hydrogen of the sulphuretted hydrogen combines with oxygen, and the liquid becomes turbid by the precipitation of sulphur. Hydrogen sulphide is an inflammable gas, burning with a bluish flame, and producing sulphur dioxide and water—

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O.$$

If mixed with oxygen in the proportion demanded by this equation, viz., two volumes of sulphuretted hydrogen and three volumes of oxygen, and ignited, the mixture explodes with violence. When the gas is burned with an insufficient supply of air or oxygen for its complete combustion, the sulphur is deposited.

Sulphuretted hydrogen is decomposed by the halogens, with the deposition of sulphur, and the formation of the hydrogen compound of the halogen element thus—

$$H_2S + Cl_2 = 2HCl + S.$$

Fluorine, chlorine, and bromine are capable of bringing about this decomposition at ordinary temperatures; in the case of iodine, the reaction is attended with absorption of heat, which may be supplied by passing the mixture of iodine vapour and sulphuretted hydrogen through a hot tube, or by causing the action to take place in the presence of water. In the latter case the heat of solution of the hydriodic acid determines the reaction.

When passed into sulphuric acid, reduction of the acid takes place with the precipitation of sulphur—

$$H_2SO_4 + H_2S = SO_2 + 2H_2O + S.$$

Sulphuretted hydrogen, therefore, cannot be dried by means of sulphuric acid.

The gas acts upon many metals with the formation of sulphides; thus, when potassium is heated in a stream of hydrogen sulphide, it readily burns and produces potassium hydrosulphide—

$$H_2S + K = KHS + H.$$

Such metals as tin, lead, silver, &c., are rapidly tarnished in contact with this gas. On this account articles of silver, when exposed to the air of towns, quickly become covered with a film of sulphide, which first appears yellowish-brown, and gradually becomes black. The discoloration of a silver spoon, when introduced into an egg which is partially decomposed, is due to the same cause.

Sulphuretted hydrogen also acts upon metallic salts, combining with the metal to form a sulphide. The "white-lead" employed in ordinary paint is gradually blackened on prolonged exposure to the air by the formation of lead sulphide.

Hydrogen sulphide is rapidly absorbed by lime, with the formation of calcium hydrosulphide—

$$CaH_2O_2 + 2H_2S = CaH_2S_2 + 2H_2O.$$

It is also absorbed by calcium sulphide, yielding the same compound. This reaction is employed in the method known as

Chance's process, for utilising the sulphur of the vat-waste of the alkali manufacture. This consists in passing lime-kiln gases through a series of vessels containing the waste mixed with water. In the first vessels the carbon dioxide is absorbed, and sulphuretted hydrogen evolved. This, passing into the later vessels, is absorbed by the vat-waste, forming calcium hydrosulphide, which in its turn is decomposed by carbon dioxide, with the evolution of twice the volume of sulphuretted hydrogen for a given volume of carbon dioxide, as in the first reaction—

$$(1)\quad CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$
$$(2)\quad CaS + H_2S = CaH_2S_2.$$
$$(3)\quad CaH_2S_2 + CO_2 + H_2O = CaCo_3 + 2H_2S.$$

The sulphuretted hydrogen, mixed with atmospheric nitrogen and a small quantity of carbon dioxide, is sufficiently rich to burn, yielding sulphur dioxide, which can then be employed for the manufacture of sulphuric acid.

Sulphuretted hydrogen is also decomposed by ferric hydroxide, with the formation of ferrous sulphide and water, and the deposition of sulphur, as described on page 401. This action takes place with the evolution of considerable heat, the temperature rising high enough to ignite a mixture of sulphuretted hydrogen and oxygen.*

Sulphuretted hydrogen is a valuable laboratory reagent, on account of the general behaviour of certain classes of sulphides. Thus, the sulphides of certain metals, being insoluble in dilute acids, are precipitated from acid solutions ; for example—

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$
$$CdCl_2 + H_2S = CdS + 2HCl.$$

Others are soluble in acids, but insoluble in alkaline liquids, and are therefore precipitated by sulphuretted hydrogen in the presence of ammonia, or by the addition of ammonium sulphide, thus—

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

A third group of metals yield sulphides that are soluble in water, and therefore are not separated either in acid or alkaline solutions.

Many of the metallic sulphides are also possessed of charac-

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* "Chemical Lecture Experiments," new ed., Nos. 577, 578.

teristic colours, which readily serve for their identification. Thus arsenious sulphide is pale yellow, and cadmium sulphide golden yellow. Antimonious sulphide has a bright red colour, while zinc sulphide is white.

This behaviour of metals towards sulphuretted hydrogen is the basis upon which certain methods of qualitative analysis are founded.

HYDROGEN PERSULPHIDE.

Formula, H_2S_2.

Modes of Formation.—(1.) This substance, which stands in the same relation to hydrogen sulphide as hydrogen peroxide does to water, may be obtained by slowly pouring a solution of calcium disulphide into hydrochloric acid in the cold, the liquids being rapidly stirred during the process of mixing, and the acid being kept in considerable excess—

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$

The hydrogen persulphide separates out as a heavy, pale-yellow, oily compound, which settles to the bottom of the liquid. The calcium disulphide is prepared by boiling together one part of lime with about twenty parts of water and one part of flowers of sulphur. The yellow liquid that is obtained will contain more or less of the higher sulphides of lime, and in proportion as these are present there will be a precipitation of sulphur with the hydrogen persulphide, thus—

$$CaS_5 + 2HCl = CaCl_2 + H_2S_2 + 3S.$$

(2.) Hydrogen persulphide may also be obtained from a compound that is produced by the action of sulphuretted hydrogen upon strychnine in the presence of oxygen—

$$2C_{21}H_{22}N_2O_2 + 6H_2S + 3O = 3H_2O + 2C_{21}H_{22}N_2O_2,3H_2S_2.$$

This substance, on treatment with an acid, yields the persulphide.

Properties.—Hydrogen persulphide is an oily liquid having a specific gravity of 1.73. It has a pungent smell, accompanied by the odour of sulphuretted hydrogen, due probably to the partial decomposition of the compound, and its vapour is irritating to the eyes. It is an unstable substance, decomposing at ordinary temperatures into sulphur and sulphuretted hydrogen; when heated, this decomposition takes place rapidly. It readily dissolves sulphur, and on this account, and the readiness with which the compound decomposes, it is extremely difficult to obtain it in a state of purity, and so to determine its exact composition. It is insoluble in water, but dissolves readily in carbon disulphide and ether; its solution in the former liquid is more stable than the liquid substance itself.

Hydrogen persulphide burns with a blue flame, yielding sulphur dioxide and water.

Hydrogen persulphide possesses feeble bleaching properties, and, like its oxygen analogue, it is decomposed by certain metallic oxides, with the evolution of sulphuretted hydrogen.

COMPOUNDS OF SULPHUR WITH CHLORINE.

Two of these compounds exist at ordinary temperatures, while a third is only known at temperatures below −22°.

1.	Disulphur dichloride or sulphothionyl chloride	S_2Cl_2.
2.	Sulphur dichloride	SCl_2.
3.	Sulphur tetrachloride	SCl_4.

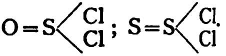
Disulphur Dichloride, S_2Cl_2.—This substance is obtained by passing dry chlorine over the surface of heated sulphur, contained in a retort; the compound, which distils away as fast as it is formed, condenses in the receiver as a yellow liquid—

$$S_2 + Cl_2 = S_2Cl_2.$$

Properties.—The redistilled liquid is an amber-coloured fuming substance with a disagreeable penetrating odour, the vapour of which irritates the eyes. Its specific gravity is 1.709, and it boils at 138.1°. In contact with water it gradually decomposes into hydrochloric acid and sulphur dioxide, with the precipitation of sulphur. The action takes place in two stages, thiosulphuric acid being formed as an intermediate product, thus—

$$(\alpha)\quad 2S_2Cl_2 + 3H_2O = 4HCl + S_2 + H_2S_2O_3.$$
$$(\beta)\quad H_2S_2O_3 = H_2SO_3 + S.$$

Disulphur dichloride dissolves sulphur with great readiness, and the solution so obtained is largely employed in the process of vulcanising indiarubber.

This compound is the most stable of the three chlorides of sulphur. From the fact that it contains chlorine and sulphur in the proportion of one atom of each element, it is sometimes called sulphur monochloride; but as its vapour-density (67.5) shows that it contains two atoms of each element in the molecule, the use of the word monochloride is calculated to mislead. The name sulphothionyl chloride indicates its analogy to thionyl chloride, $SOCl_2$, from which it may be regarded as being derived, by the replacement of the oxygen by an atom of sulphur,  $O=S\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix}$; $S=S\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix}$

Sulphur Dichloride, SCl_2.—This compound is obtained by passing a stream of dry chlorine into disulphur dichloride at a temperature not above 0°. When the maximum amount of chlorine is absorbed, the liquid assumes a dark reddish-brown colour. Excess of chlorine is removed by passing a stream of carbon dioxide through the liquid.

Sulphur dichloride rapidly dissociates with rise of temperature into free chlorine and disulphur dichloride; at +20° this decomposition amounts to 6.5 per cent., at 50°, 24.59 per cent., and at 100°, 80.85 per cent. On boiling the compound, therefore, chlorine is evolved, and the disulphur dichloride remains behind.

In contact with water it is decomposed in the same manner as the more stable compound.

Sulphur Tetrachloride, SCl_4.—This compound only exists at temperatures below −22°, and is produced by saturating sulphur dichloride with chlorine at that temperature. It dissociates very rapidly as the temperature rises; thus, at 7° above the temperature at which it is formed, viz., at −15°, this decomposition amounts to 58.05 per cent. At −2°, 88.07 per cent. of the compound dissociates, while at +6.2° the percentage rises to 97.57.

The compound is decomposed by water with violence into sulphur dioxide and hydrochloric acid—

$$SCl_4+2H_2O=SO_2+4HCl.$$

Compounds of Sulphur with Bromine and Iodine have been obtained, corresponding to S_2Cl_2. S_2Br_2 as a red-coloured liquid, boiling with partial decomposition at 200°; and S_2I_2 as a dark-grey crystalline solid, which melts at a temperature about 60°.

OXIDES AND OXYACIDS OF SULPHUR.

Four oxides of sulphur are known, namely—

(1.) Sulphur sesquioxide (hyposulphurous anhydride)	S_2O_3.
(2.) Sulphur dioxide (sulphurous anhydride) . .	SO_2.
(3.) Sulphur trioxide (sulphuric anhydride) . .	SO_3.
(4.) Persulphuric anhydride	S_2O_7.

These four oxides give rise respectively to the four acids, hyposulphurous, sulphurous, sulphuric, and persulphuric, besides which several other sulphur acids are known—

Hyposulphurous acid	$H_2S_2O_4$	$\left.\begin{matrix}HO{\cdot}SO\\HO{\cdot}SO\end{matrix}\right\}$
Sulphurous acid	H_2SO_3	$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO.$
Sulphuric acid	H_2SO_4	$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$
Persulphuric acid	HSO_4*	$\left.\begin{matrix}HO\\O\end{matrix}\right\}SO_2.$
Thiosulphuric acid †	$H_2S_2O_3$	$\left.\begin{matrix}HO\\HS\end{matrix}\right\}SO_2.$
Pyrosulphuric acid (Nordhausen sulphuric acid)	$H_2S_2O_7$	$\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}O.$

Besides these acids, there is a series known under the general name of the polythionic acids. They may be regarded as being derived from dithionic acid, which is the first of the series, by the absorption into the molecule of various quantities of sulphur. Four of these acids are believed to exist, viz. :—

Dithionic acid (sometimes called hyposulphuric acid) . . .	$H_2S_2O_6$	$\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}$
Trithionic acid	$H_2S_3O_6$	$\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}S.$
Tetrathionic acid	$H_2S_4O_6$	$\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}S_2.$
Pentathionic acid	$H_2S_5O_6$	$\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}S_3.$

SULPHUR DIOXIDE.

Formula, SO_2. Molecular weight = 64.06. Density = 32.03.

Occurrence.—This compound is met with in the gaseous emanations from volcanoes, and in solution in certain volcanic springs. It is also present in the air of towns, being derived from the combustion of the sulphur compounds present in coal.

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* By some chemists— $H_2S_2O_8$, $\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}O_2.$

† This acid is sometimes incorrectly called *hyposulphurous acid*, its sodium salt being known as *sodium hyposulphite:* the so-called "hypo" of the photographers.

Modes of Formation.—(1.) Sulphur dioxide is formed when sulphur burns in air or oxygen—

$$S+O_2=SO_2.$$

At the same time small quantities of sulphur trioxide are formed, which render the gas obtained by this combustion more or less foggy.

(2.) Sulphur dioxide may also be obtained by heating sulphur with a metallic peroxide, such as manganese dioxide, thus—

$$S_2+MnO_2=SO_2+MnS.$$

(3.) It is obtained when such metallic sulphides as copper pyrites or iron pyrites are roasted in a current of air, the metal being converted into oxide, thus—

$$2FeS_2+11O=Fe_2O_3+4SO_2.$$

(4.) The most convenient laboratory process for preparing sulphur dioxide consists in heating sulphuric acid with copper, the final products of the reaction being copper sulphate, water, and sulphur dioxide *—

$$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O.$$

The metals mercury or silver may be substituted for copper, but in practice the latter metal is usually employed.

(5.) Sulphur dioxide is also formed when sulphuric acid is heated with sulphur, the oxidation of the sulphur and the reduction of the sulphuric acid going on simultaneously—

$$S+2H_2SO_4=2H_2O+3SO_2.$$

(6.) The reduction of sulphuric acid may be brought about by means of carbon; thus, if sulphuric acid be heated with carbon, the latter is oxidised to carbon dioxide, and the acid is reduced to sulphur dioxide—

$$C+2H_2SO_4=2H_2O+2SO_2+CO_2.$$

This method is employed on a large scale for the preparation of alkaline sulphides. The carbon dioxide which accompanies the sulphur dioxide, not being soluble to any extent in water containing sulphurous acid, is not in any way detrimental.

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* Secondary reactions go on simultaneously, resulting in the formation of black cuprous sulphide—

$$5Cu+4H_2SO_4=3CuSO_4+4H_2O+Cu_2S.$$

(7.) Sulphur dioxide is formed by the decomposition of a sulphite by dilute sulphuric acid, thus—

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

Properties.—Sulphur dioxide is a colourless gas, having the well-known suffocating smell usually associated with burning sulphur. The gas will not burn in the air, nor will it support the combustion of ordinary combustibles : a taper introduced into the gas is instantly extinguished. Sulphur dioxide is more than twice as heavy as air, its specific gravity being 2.211 (air = 1). On this account it is readily collected by displacement; it cannot be collected over water on account of its solubility in that liquid, but may be collected over mercury. The solubility of sulphur dioxide in water at various temperatures is seen by the following figures—

1 vol. of water at 0° dissolves 79.789 vols. SO_2.
" " 20° " 39.374 "
" " 40° " 18.766 "

The solution is strongly acid, and is regarded as sulphurous acid, the gas having entered into chemical union with the water—

$$SO_2 + H_2O = H_2SO_3.$$

On cooling a saturated solution of sulphur dioxide to 0°, a solid crystalline hydrate is deposited, having the composition H_2SO_3, $8H_2O$.*

When the solution is boiled the whole of the sulphur dioxide is expelled.

Sulphur dioxide is an easily liquefied gas. At 0° a pressure of 1.53 atmospheres is sufficient to condense it, while at ordinary pressures it may be liquefied by a cold of $-10°$. Its critical temperature is 155.4°.

To obtain liquid sulphur dioxide, the gas, as evolved from the action of sulphuric acid upon copper, is dried by being passed through a bottle containing sulphuric acid, and is then passed through a gas-condensing tube (Fig. 113) immersed in a freezing-mixture. The gas at once condenses in the bulb of the apparatus as a colourless, transparent, mobile liquid, which boils at $-8°$. When the liquid is cooled to $-76°$ it solidifies to a transparent, ice-like mass.

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* Several hydrates of sulphurous acid have been obtained, $H_2SO_3,6H_2O$; $H_2SO_3 10H_2O$; $H_2SO_3,14H_2O$.

Liquid sulphur dioxide is largely employed as a refrigerating agent, low temperatures being obtained by its rapid evaporation under reduced pressure. The liquid dissolves phosphorus, iodine, sulphur, and many resins. When thrown upon water a portion of the liquid dissolves, and owing to the reduction of temperature caused by the rapid evaporation of the remainder, a quantity of the water is frozen. The ice so produced contains a large proportion of the solid hydrate, $H_2SO_3,8H_2O$.

Although sulphur dioxide is incapable of supporting the combustion of ordinary combustibles, many metals will take fire and burn when heated in the gas. Thus, when finely divided iron is heated in a stream of sulphur dioxide it burns, forming sulphide and oxide of the metal.

FIG. 113.

It also unites with many metallic peroxides, and often with so much energy as to give rise to light and heat. Thus, when passed over peroxide of lead, the mass glows spontaneously in the gas, and lead sulphate is produced—

$$PbO_2+SO_2=PbSO_4.$$

Or if sodium peroxide is dusted into a cylinder of the gas, the peroxide burns with a brilliant light, yielding sodium sulphate—

$$Na_2O_2 + SO_2 = Na_2SO_4.$$

Sulphur dioxide is decomposed by the influence of strong light. If a concentrated beam of electric light be passed through a vessel filled with gaseous sulphur dioxide, the gas at first will appear perfectly transparent and clear ; but in the course of a few minutes the track of the beam will become more and more visible as it traverses the gas, owing to the formation of thin clouds of sulphur trioxide and sulphur, until the atmosphere of the vessel appears to be filled with fog (Fig. 114)—

$$3SO_2 = 2SO_3 + S.$$

After the lapse of a short time, if the vessel be removed from the strong light, the atmosphere will once more become clear, owing to the reformation of sulphur dioxide.

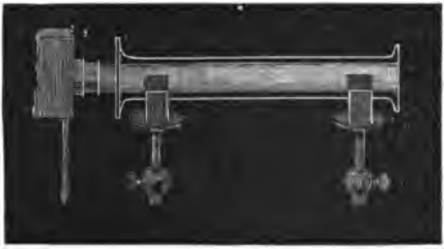

FIG. 114.

Sulphur dioxide possesses powerful bleaching properties when in the presence of water. Its bleaching action is due to its absorption of oxygen from water, and consequent liberation of hydrogen, thus—

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

The hydrogen so set free reduces the colouring-matter, with the formation of colourless compounds : the action in this case being the reverse to that which takes place with chlorine. In some instances, the bleaching is due to the formation of a colourless compound, by the direct combination of sulphur dioxide with the colouring-matter, as the original colour may often be restored by treatment with dilute sulphuric acid, or by weak alkaline solutions.

Thus, by passing sulphur dioxide into an infusion of rose leaves, the red colour of the liquid is quickly discharged, but on the addition of a small quantity of sulphuric acid the colour is restored.

Sulphur dioxide is employed in bleaching materials that would be injured by exposure to chlorine, such as straw, silk, wool, sponge, &c., and the familiar yellow colour which gradually comes over a sponge or a piece of bleached flannel when it is washed with soap is an illustration of the power of alkalies to restore the original colour to materials that have been bleached by this substance.

In the presence of water sulphur dioxide converts chlorine into hydrochloric acid, and on this account is employed as an "antichlor"—

$$SO_2 + 2H_2O + Cl_2 = 2HCl + H_2SO_4.$$

In the same way it acts upon iodine, with the formation of hydriodic acid—

$$SO_2 + 2H_2O + I_2 = 2HI + H_2SO_4.$$

In the case of iodine, however, this reaction only takes place when a certain degree of dilution is maintained, for in a more concentrated condition sulphuric acid is reduced by hydriodic acid into sulphur dioxide, according to the reverse equation, thus—

$$H_2SO_4 + 2HI = I_2 + 2H_2O + SO_2.$$

It has been shown * that aqueous sulphurous acid can only be completely oxidised by iodine, as indicated in the former equation, when the proportion of sulphur dioxide does not exceed 0.05 per cent.; when the amount exceeds this proportion the second reaction comes into operation.

Sulphur dioxide brought into contact with iodic acid, or an iodate, is oxidised into sulphuric acid and liberates iodine, thus—

$$2HIO_3 + 4H_2O + 5SO_2 = 5H_2SO_4 + I_2.$$

This reaction is made use of as a method for the detection of the presence of sulphur dioxide. Paper which has been moistened with a solution of potassium iodate and starch, on exposure to sulphur dioxide is at once turned blue, owing to the liberated iodine combining with the starch.

The composition of sulphur dioxide may be determined by the combustion of sulphur in a measured volume of oxygen, in the apparatus employed for showing the volume composition of carbon dioxide (Fig. 67). After the fragment of sulphur has burnt, and the apparatus has been allowed to cool, it will be seen that there is no alteration in the volume of the contained gas—the sulphur

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* Bunsen.

dioxide produced occupying the same volume as the oxygen used in its formation. Sulphur dioxide, in other words, contains its own volume of oxygen. One molecule, therefore, of sulphur dioxide contains one molecule of oxygen, weighing 32. But the molecular weight of sulphur dioxide is 64.06; therefore $64.06 - 32 = 32.06$ = the weight of sulphur contained in the molecule of the gas. Sulphur dioxide, therefore, contains in the molecule one atom of sulphur combined with two atoms of oxygen, hence its composition is expressed by the formula SO_2.

Sulphurous Acid and Sulphites.—Sulphurous acid is only known in solution and in its hydrates. The solution smells of sulphur dioxide, and gradually undergoes decomposition by absorption of oxygen. The acid is dibasic, having two atoms of hydrogen replaceable by metals; it is therefore capable of forming two series of salts, according to whether one or both of the hydrogen atoms are replaced. Thus, by its action upon potassium hydroxide, when the acid is in excess, the so-called acid potassium sulphite, or hydrogen potassium sulphite, is obtained—

$$KHO + H_2SO_3 = H_2O + HKSO_3.$$

Whereas, if the metallic hydroxide be in excess, the normal potassium sulphite is formed—

$$2KHO + H_2SO_3 = 2H_2O + K_2SO_3.$$

The alkaline sulphites are readily soluble in water, all other normal sulphites being either difficult of solution or insoluble.

SULPHUR TRIOXIDE.

Formula, SO_3. Molecular weight = 80.06. Vapour density = 40.03.

Modes of Formation.—(1.) This compound is produced when a mixture of sulphur dioxide and oxygen is passed over heated spongy platinum or platinised asbestos—

$$2SO_2 + O_2 = 2SO_3.$$

On leading the product through a well-cooled receiver, the sulphur trioxide condenses in white silky needles. This method has been successfully employed on a commercial scale. The mixture of sulphur dioxide and oxygen is obtained by allowing ordinary strong sulphuric acid to drop into earthenware retorts heated to bright redness, whereby it is almost entirely broken up into these two gases and water, thus—

$$H_2SO_4 = SO_2 + O + H_2O.$$

The gases are then deprived of the water, by passage first through a condenser, and then through a leaden tower containing coke moistened with sulphuric acid, and are finally passed over heated platinised asbestos contained in glazed earthenware pipes.

(2.) Sulphur trioxide is most conveniently obtained by gently heating pyrosulphuric acid in a glass retort. The trioxide distils over and may be collected in a well-cooled receiver—

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

(3.) It may also be obtained by heating sodium pyrosulphate to bright redness—

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

The sodium pyrosulphate is produced when hydrogen sodium sulphate (so-called *bisulphate of soda*) is heated to about 300°, thus—

$$2HNaSO_4 = H_2O + Na_2S_2O_7.$$

And on account of this origin it is sometimes termed *anhydrous sodium bisulphate.*

(4.) Sulphur trioxide can also be produced by the action of phosphorus pentoxide upon sulphuric acid. This most powerful dehydrating substance withdraws from the sulphuric acid the elements of water when gently heated, thus—

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

The trioxide is distilled from the mixture, and the metaphosphoric acid remains in the retort.

Properties.—Sulphur trioxide is a white, silky-looking, crystalline substance, which melts at 14.8° and boils at 46°. It is very volatile, and gives off dense white fumes in contact with air, owing to the combination of its vapour with atmospheric moisture to form sulphuric acid. It combines with water with great energy to form sulphuric acid; a fragment of the compound dropped into water dissolves with a hissing sound resembling the quenching of red-hot iron—

$$SO_3 + H_2O = H_2SO_4.$$

When brought in contact with the skin, or other organic matter containing hydrogen and oxygen, it abstracts these elements and produces a burnt or charred effect upon the substance. Sulphur trioxide unites directly with barium oxide, BaO, and if the baryta be dry the mass becomes incandescent, owing to the heat of the union, and barium sulphate is formed—

$$BaO + SO_3 = BaSO_4.$$

When the vapour of sulphur trioxide is passed through a red-hot tube, it is broken down into sulphur dioxide and oxygen.

When the trioxide is heated, it melts to a colourless liquid, which exhibits a remarkably high rate of expansion by heat; between 25° and 45° its mean coefficient of expansion is 0.0027, nearly three-fourths of the expansion coefficient of a gas.

Sulphur Sesquioxide, S_2O_3.—A solution of this compound in fuming sulphuric acid was obtained early in the century by heating flowers of sulphur with Nordhausen sulphuric acid, whereby a blue solution was obtained. The substance may be prepared by the gradual addition of dry flowers of sulphur to melted sulphur trioxide, at a temperature just above its melting-point, when a malachite-green crystalline solid separates out.

The compound is unstable at ordinary temperatures, being resolved into sulphur dioxide and sulphur, the decomposition taking place rapidly upon gently warming—

$$2S_2O_3 = S + 3SO_2.$$

If the sesquioxide be sealed up in a bent glass tube and gently warmed, the sulphur dioxide may be obtained liquid in one limb of the tube.

Hyposulphurous Acid,* $H_2S_2O_4$.—This compound was discovered by Schützenberger, who gave to it the formula H_2SO_2. The later investigations of Bernsthen prove that its composition is expressed by the formula $H_2S_2O_4$. It is obtained by the reduction of sulphurous acid by means of nascent hydrogen. Thus, when zinc is acted upon by an aqueous solution of sulphurous acid, no hydrogen is evolved, as the nascent gas combines with oxygen of the acid to form water—

$$2H_2SO_3 + 2H = 2H_2O + H_2S_2O_4.$$

The solution so obtained has a yellowish colour, and possesses powerful reducing and bleaching properties.

Sodium hyposulphite ($Na_2S_2O_4$) may be obtained by the action of zinc upon a cooled concentrated solution of hydrogen sodium sulphite ($HNaSO_3$), air being carefully excluded, a double sulphite of sodium and zinc being at the same time produced, thus—

$$4HNaSO_3 + Zn = Na_2S_2O_4 + Na_2SO_3.ZnSO_3 + 2H_2O.$$

The greater part of the double sodium-zinc sulphite is deposited as crystals, the rest is removed by adding to the mother-liquor about four times its volume of alcohol, in a closed flask. The double salt, being less soluble in alcohol than the hyposulphite, is first deposited, and the clear liquid after being poured off and corked up, is cooled, when it solidifies to a mass of crystals of nearly pure sodium hyposulphite. The crystals in the wet condition are rapidly oxidised on exposure to air; but if quickly pressed between blotting-paper and dried in vacuo, the dry salt is not acted upon by atmospheric oxygen.

The acid is obtained from the sodium salt by the action upon it of oxalic acid.

Sodium hyposulphite is also formed when a solution of hydrogen sodium sulphite is subjected to electrolysis, the nascent hydrogen developed at the negative electrode reducing the sulphite to hyposulphite by the abstraction of one atom of oxygen.

Properties.—Hyposulphurous acid is an extremely unstable, yellow-coloured liquid which rapidly decomposes into sulphur dioxide, water, and sulphur—

$$2H_2S_2O_4 = 3SO_2 + 2H_2O + S,$$

a certain quantity of thiosulphuric acid being formed as an intermediate product at the same time—

$$2H_2S_2O_4 = H_2S_2O_3 + 2SO_2 + H_2O.$$

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* This compound (sometimes called *hydrosulphurous* acid) must not be confounded with thiosulphuric acid, which is often incorrectly called hyposulphurous acid (page 435).

The acid reduces salts of silver or mercury, with precipitation of the metal, thus—

$$HgCl_2+2H_2O+H_2S_2O_4=Hg+2HCl+2H_2SO_3.$$

The sodium salt possesses the same bleaching and reducing powers as the acid, and when wet or in solution it rapidly absorbs oxygen from the air and is converted into a compound known as *sodium metabisulphite*—

$$Na_2S_2O_4+O=Na_2S_2O_5.$$

The relation in which these two compounds stand to each other will perhaps be more evident if their formulæ are written thus—

$$\left.\begin{matrix}NaO{\cdot}SO\\NaO{\cdot}SO\end{matrix}\right\}+O=\left.\begin{matrix}NaO{\cdot}SO\\NaO{\cdot}SO\end{matrix}\right\}O.$$

PERSULPHURIC ANHYDRIDE.

Formula, S_2O_7.

This compound is formed when a mixture of dry sulphur dioxide and oxygen is subjected to the silent electric discharge in an ozone tube, or by treating sulphur trioxide and oxygen in the same manner. At the end of some hours a small quantity of a viscous liquid collects upon the walls of the glass vessel, which, when cooled, solidifies in the form of long transparent needle-shaped crystals resembling sulphur trioxide in appearance. It is a very unstable substance, and can only be preserved a short time even at low temperatures. It is soluble in water, with the formation of persulphuric acid, but the solution rapidly undergoes decomposition into oxygen and sulphuric acid—

$$S_2O_7+H_2O=2HSO_4.$$
$$2HSO_4+H_2O=2H_2SO_4+O.$$

When very gently warmed, persulphuric anhydride rapidly breaks up into sulphur trioxide and oxygen—

$$S_2O_7=2SO_3+O.$$

The readiness with which it gives up oxygen constitutes this compound a powerful oxidising agent, and affords the clue to most of its reactions.

Persulphuric Acid and Persulphates.—When dilute sulphuric acid is subjected to electrolysis (as in the process commonly spoken of as the *electrolysis of water*), appreciable quantities of persulphuric acid are found in solution at the positive electrode or anode.

The acid itself has never been obtained in a state of purity, its aqueous solution rapidly undergoing decomposition, as already mentioned.

In solution this compound displays all the oxidising properties of the oxide.

The potassium salt may be obtained by the electrolysis of a saturated solution of hydrogen potassium sulphate in a divided cell, the action being due to the oxidation of the hydrogen potassium sulphate by the nascent oxygen developed at the anode, thus—

$$2HKSO_4+O=H_2O+2KSO_4.$$

The potassium persulphate, being a sparingly soluble salt, crystallises out, and may be freed from the acid sulphate by recrystallisation.

The ammonium salt, NH_4SO_4, and the barium salt, $Ba(SO_4)_2,4H_2O$, have also been obtained. Barium persulphate is soluble in water, being much more readily dissolved than the potassium salt; thus, 100 parts of water at 0° dissolve 1.77 parts of potassium persulphate and 52.2 parts of the barium salt. On this account solutions of persulphates give no precipitate with barium chloride, whereby they are distinguished from sulphates; if the mixture be warmed, however, the persulphate is decomposed into a sulphate, with evolution of chlorine, thus—

$$2KSO_4 + BaCl_2 = Ba(SO_4)_2 + 2KCl = BaSO_4 + K_2SO_4 + Cl_2.$$

In the solid condition the persulphates are stable salts, but their aqueous solutions gradually evolve oxygen and become converted into sulphates—

$$2KSO_4 + H_2O = 2HKSO_4 + O.$$

The reactions exhibited by solutions of persulphates are those of strong oxidising agents.

SULPHURIC ACID.

Formula, H_2SO_4.

Modes of Formation.—(1.) This acid is formed when sulphur trioxide is dissolved in water—

$$SO_3 + H_2O = H_2SO_4.$$

(2.) It is also formed by the direct union of sulphur dioxide with hydrogen peroxide—

$$SO_2 + H_2O_2 = H_2SO_4.$$

(3.) An aqueous solution of sulphur dioxide gradually absorbs oxygen, and is converted into sulphuric acid—

$$H_2SO_3 + O = H_2SO_4.$$

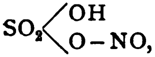
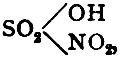
(4.) **Manufacture of Sulphuric Acid.**—Sulphur dioxide is unable to absorb an additional atom of oxygen, and so pass into sulphur trioxide, without the aid of some third substance which can act as a catalytic agent or a carrier of oxygen. The material which is employed for this purpose in the process by which sulphuric acid is manufactured is one of the oxides of nitrogen, which is capable of giving up oxygen to the sulphur dioxide, and of again taking up oxygen from the air. Thus, nitrogen peroxide (NO_2), by the loss of one atom of oxygen, is reduced to nitric oxide, NO; which in its turn combines with atmospheric oxygen and is reconverted into nitrogen peroxide. Therefore, when sulphur dioxide and oxygen are mixed with nitrogen peroxide in the presence of steam, a series of reactions takes place, the final result of which is that the oxygen is caused to combine with the sulphur dioxide and water, with the formation of sulphuric acid—

$$SO_2 + O + H_2O = H_2SO_4.$$

The nitrogen peroxide at the end of the reaction is unchanged, and is able to react in the same series of changes over and over again, thus transforming, theoretically, an unlimited, and, in practice, a relatively large quantity of sulphur dioxide into sulphuric acid.

The series of changes that gives rise to the ultimate product is the following :—The sulphur dioxide, nitrogen peroxide, and water give rise, in the first place, to the formation of nitro-sulphonic acid and a molecule of nitric oxide—

$$(1.)\ 2SO_2+3NO_2+H_2O=2H(NO)SO_4+NO.$$

Nitro-sulphonic acid (sometimes called *nitro-sulphuric acid*, and *nitrosyl sulphate*) may be regarded as sulphuric acid in which one of the hydrogen atoms is replaced by the group (NO), thus,  $SO_2\left<\begin{matrix}OH\\O-NO,\end{matrix}\right.$ in which case the nitrogen is linked to the sulphur by the intervention of oxygen ; or it may be considered as derived from sulphuric acid by the replacement of one of the groups (HO) by the group NO_2,  $SO_2\left<\begin{matrix}OH\\NO_2,\end{matrix}\right.$ when the nitrogen is directly attached to the sulphur. The substance is a white crystalline compound which in the presence of water is instantly decomposed into sulphuric acid and a mixture of nitric oxide and nitrogen peroxide, thus—

$$(2.)\ 2SO_2(HO)(NO_2)+H_2O=2H_2SO_4+NO+NO_2.$$

The nitric oxide in this and the former reaction, on coming in contact with the atmospheric oxygen, is at once reconverted into nitrogen peroxide—

$$(3.)\ NO+O=NO_2.$$

In the process of the manufacture the crystalline compound $SO_2(HO)(NO_2)$ (known as *chamber crystals*) is not actually isolated, unless from accidental causes the supply of water is in deficit, the production of these crystals being regarded as an indication that the process is not being well carried out.

The formation of sulphuric acid by these reactions, with the intermediate production of the chamber crystals, may be carried out on a small scale by means of the apparatus shown in Fig. 115. A large flask, F, is fitted with a cork, through which pass five tubes : three of these are connected to separate two-necked bottles containing sulphuric acid, through which can be delivered respectively, nitric oxide, sulphur dioxide, and oxygen. The fourth tube is attached to a flask in which water may be boiled, and through which oxygen can be passed, and the fifth tube (not shown in the figure) serves as an exit. A quantity of oxygen is first passed into the large flask through the drying-bottle D, and sufficient nitric oxide is then allowed to enter, to form deep red vapours ; at the same time sulphur dioxide is passed in through the bottle S. In order to introduce a small quantity of moisture, oxygen is allowed to enter through the flask of boiling water, and in a few moments large white crystals begin to form all over the interior of the flask, and rapidly spread until the whole surface is covered.

In order to show the second reaction in the cycle, the gaseous contents of the flask may be swept out by means of a rapid stream of oxygen passed in through the drying-bottle D ; and when the atmosphere within the apparatus is colourless, a quantity of steam is driven in from the small flask. The chamber crystals will be seen to dissolve with effervescence, and the flask once more becomes filled with brown fumes. The nitric oxide evolved by the decomposition of the nitrosyl sulphate, coming in contact with the oxygen within the flask, at once regenerates nitrogen peroxide, in accordance with equation No. 3.

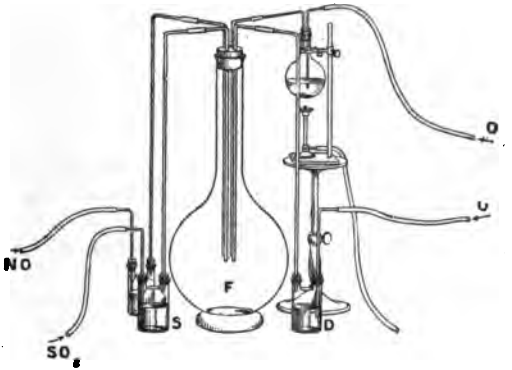


FIG. 115.

The solution formed in the flask will be found to yield a precipitate of barium sulphate, on the addition to it of a soluble barium salt.

On a manufacturing scale, the combination of the reacting gases and vapours which gives rise to the sulphuric acid takes place in large leaden chambers, usually about 100 feet long, 25 feet wide, and 20 feet high, having therefore a capacity of 50,000 cubic feet, several of such chambers being placed in series. Into these chambers there is delivered sulphur dioxide, air, oxides of nitrogen, and steam.

The plant employed for the manufacture of sulphuric acid consists broadly of four parts. 1. Apparatus for generating sulphur dioxide. 2. Apparatus for producing oxides of nitrogen. 3. Apparatus for absorbing oxides of nitrogen from the gases leaving the chambers. 4. The chambers in which the reactions are made.

(1.) *Pyrites Burners.*—The sulphur dioxide is obtained either by burning native sulphur, or roasting the "spent oxide" of the gas works (see Sulphur), or by roasting pyrites, the latter being the most general method. The pyrites burner (Fig. 116, B) is essentially a small furnace or kiln in which the ore is heated, and in which the admission of air can be duly regulated, as not only is it necessary to admit sufficient air to completely burn the whole of the sulphur, and so prevent any volatilisation of it in an unburnt condition, but also to supply the requisite volume of oxygen for the requirements of the reactions which are to go on within the chamber. Too large a volume of air must be avoided, in order not to unduly dilute the chamber gases.

(2.) If no loss of nitrogen peroxide took place during the cycle of changes, the same quantity of this gas would convert an infinite amount of sulphur dioxide and water into sulphuric acid, but in practice, owing to leakage, defective absorption, and the reduction of a certain percentage of this compound into nitrous oxide, it is necessary to constantly replenish the supply. This is usually done by generating a small quantity of nitric acid (by the action of sulphuric acid upon nitre) in earthenware pots, which are usually placed in an enlarged part of the flue of the pyrites burner, known as the "nitre oven," and which is provided with a door for the introduction of the pots (Fig. 116, N). The heated gases playing upon these pots promotes the evolution of the nitric acid, which in contact with sulphur dioxide is at once decomposed according to the equation—

$$2HNO_3+SO_2=H_2SO_4+2NO_2.$$

It is found that to make up for the loss of nitrogen peroxide, about three to four parts of nitre are required for every 100 parts of sulphur burnt as pyrites.

(3.) The apparatus for the absorption of the nitrogen peroxide from the gases that are drawn from the chamber at the end of the series is known as the "Gay-Lussac Tower" (Fig. 116, T). This consists of a square leaden tower filled with fragments of coke, and down which there is caused to slowly percolate a stream of cold strong sulphuric acid, the acid being evenly spread over the mass of coke by a special distributing arrangement. The nitrogen peroxide is absorbed by the acid, with the formation of nitro-sulphonic acid, $SO_2(HO)(NO_2)$. In order to make use of the absorbed nitroxygen compound, the acid which flows from the Gay-Lussac tower is pumped to the top of another very similar tower, situated between the "burners" and the first of the chambers, and known as the "Glover Tower," G. The hot gases from the burners, consisting of sulphur dioxide, nitrogen, and oxygen, together with the small quantities of nitrogen peroxide from the nitre pots, are made to pass up this tower on their way to the first chamber, and meeting with the descending stream of nitro-sulphonic acid as it runs over the bricks or flints with which the tower is filled, denitrification of the latter takes place, thus—

$$2SO_2(HO)(NO_2)+SO_2+2H_2O=2NO+3SO_2(HO)(HO),$$
$$\text{or } 3H_2SO_4.$$

The nitric oxide thus evolved, in presence of the atmospheric oxygen, is converted into nitrogen peroxide, and swept along with the other gases into the chambers.

In practice it is usual to deliver down the Glover tower, besides the nitro-sulphonic acid, a quantity of "chamber acid" from a separate tank. The effect of the heated gases upon this dilute acid is to remove a portion of the water from it, thereby effecting its partial concentration, and furnishing the water demanded by the above equation. It will be seen, therefore, that there is a scrubber tower at each end of the series of chambers, the "Gay-Lussac" at the exit, where nitrogen peroxide is absorbed; and the "Glover" at the commencement, where the dissolved nitrogen compound is again liberated and returned to the chambers.

(4.) The chambers are made of sheet lead, connected together by fusing the edges by means of an oxyhydrogen flame, without the intervention of solder, as the presence of another metal gives rise to the rapid corrosion of the lead on account of galvanic action being set up; this method of joining the lead is known as *autogenous soldering*. The enormous leaden chamber is supported in a framework of wood, to which the lead is secured by bands of the same metal, and the whole is usually supported on iron or brick pillars.

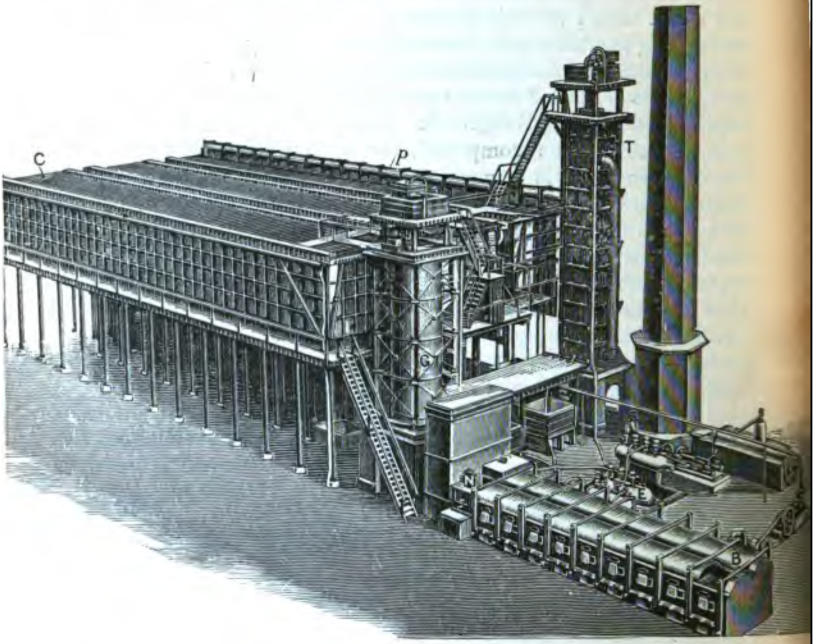


FIG. 116.

B.—Double row of pyrites burners, placed back to back: one being shown open.
N.—Hearth where the nitre pots are placed: one shown as open.
G.—Glover Tower, with two tanks at top: one for the nitro-sulphuric acid derived from the Gay-Lussac tower, the other for the "chamber acid." These acids are forced up from the leaden vessels E, called "eggs."
C.—Leaden chamber, of which there are three shown in the figure.
P.—Pipe conveying the gases from the third chamber to the Gay-Lussac tower.
T.—Gay-Lussac Tower. The tanks at the top of this and the Glover tower are enclosed in wooden sheds.

The general arrangement of a modern sulphuric acid works is seen in Fig. 116. The gases from the double row of pyrites burners B are led through the Glover tower G, where they effect the denitrification of the nitro-sulphonic acid, as already explained. From this tower they are delivered into the series of chambers, where they meet with the necessary supply of steam. The acid collects upon the floor of the chambers, and samples are constantly drawn off by means of an arrangement known as a *drip-pipe*, which, acting in a manner similar to a rain gauge, indicates the progress of the processes going on within. The gases, after being drawn through the entire series of chambers by means of the draught caused by the tall chimney, are finally passed up the Gay-Lussac tower T, where all the nitrogen peroxide is absorbed, and returned to the chambers through the intervention of the Glover tower G, as above described.

The acid which collects in the chambers is usually not permitted to reach a higher specific gravity than about 1.6, when it contains about 68 per cent. of sulphuric acid; for if the strength be allowed to exceed this, the acid not only begins to dissolve the nitrogen peroxide in the chamber, but exerts a corrosive action upon the lead of which the chamber is constructed. It is therefore withdrawn, and the first stage in the further concentration is effected either by the action of the Glover tower, or by evaporation in shallow leaden pans.

In order to bring up the strength of the acid to that of "oil of vitriol," that is, to about 98 per cent., the acid from the Glover tower or the leaden pans is heated in either glass or platinum stills.

Sulphuric acid, unless specially purified, is liable to contain a number of impurities, such as lead sulphate, derived from the action of the acid upon the chamber; arsenic, from the pyrites employed; oxides of nitrogen, and sulphur dioxide. From most of the impurities, except the arsenic, the acid may be purified by the addition of ammonium sulphate, and subsequent redistillation—

$$(NH_4)_2SO_4+2SO_2(HO)(NO_2)=3H_2SO_4+2H_2O+2N_2.$$

Arsenic is removed by precipitation of the sulphide, by means of sulphuretted hydrogen, from the acid in a moderately dilute state.

(5.) *The "Contact Process."* As already stated, when a mixture of sulphur dioxide and oxygen is brought into contact with finely divided platinum, the metal acts the part of a carrier, or catalytic agent, and causes the union of the gases. By absorbing the sulphur trioxide so produced in water, sulphuric acid is obtained.

The chief obstacles to the successful utilisation of this reaction on a manufacturing scale are the impurities present in the sulphur dioxide derived from the pyrites burners, which are found to rapidly destroy the effectiveness of the platinum. By the system of purification now adopted these difficulties have been removed, and the operation is being conducted on a successful manufacturing scale.

In outline the process is the following. The mixture of sulphur dioxide and air drawn from the pyrites burners is first passed through a chamber called the "dust chamber," into which jets of steam can be injected. This serves the twofold purpose of removing dust carried mechanically from the burner, and of diluting and partially removing the sulphuric acid which is also a product of the burner. The gases after being sufficiently cooled are then made to pass up through a series of towers (resembling Glover towers) where they meet a descending spray of water. They are next dried by passing up another tower (which may be compared to the Gay-Lussac tower), where they meet a descending stream of strong sulphuric acid. The gases are then admitted to the contact chamber, which consists of a vessel containing a number of small perforated shelves upon which is spread a layer of platinised asbestos. The shelves are arranged one above the other in tall narrow columns which are separated from each other in the chamber by a slight space, the object being to prevent the mass from locally overheating during the operation.

At the commencement the vessel is gently heated by gas jets, but when the operation has once started external heat is withdrawn, and care is then required to prevent the temperature rising above about 350° (which is found to be the most favourable temperature) owing to the heat of union of sulphur dioxide and oxygen.

Properties.—Sulphuric acid is a perfectly colourless, heavy, oily liquid. The acid obtained by distillation always contains about 2 per cent. of water; stronger than this it cannot be prepared by evaporation or distillation. When, however, acid of this strength is cooled to 0°, colourless crystals of pure sulphuric acid, containing 100 per cent. H_2SO_4, are deposited. The crystals melt at 10.5°, and remain liquid at temperatures much below this point. The specific gravity of the pure acid is 1.854 at 0°. When boiled it gives off sulphur trioxide until the amount of water in it rises to 1.5 per cent., when it distils unchanged at a temperature of 338°.

Sulphuric acid has a powerful affinity for water, and absorbs moisture from the atmosphere with great readiness. On this account it constitutes one of the most valuable desiccating agents, and is constantly made use of for depriving gases, upon which it exerts no chemical action, of aqueous vapour. Owing to its strong affinity for water it decomposes many organic substances containing hydrogen and oxygen, withdrawing from the compounds these elements in the proportion to yield water; its action upon formic acid, oxalic acid (see Carbon Monoxide), and alcohol (see Ethylene) are examples of this action.

When the acid is poured upon such substances as wood or sugar the elements composing water are withdrawn and the carbon is liberated, with the result that the compounds are blackened or charred.

When sulphuric acid is mixed with water considerable heat is disengaged, the temperature often rising to the boiling-point of water, and at the same time a diminution in volume takes place. The maximum contraction is obtained upon mixing the materials in the proportion of one molecule of acid to two molecules of water. The diminution in volume in this case amounts to 8 per cent., and the composition of the acid produced corresponds to the formula $H_2SO_4,2H_2O$.

Sulphuric acid combines with water in various proportions, forming a number of hydrates of a more or less definite character. The best known are those represented by the formulæ H_2SO_4,H_2O and $H_2SO_4,2H_2O$. These compounds may be regarded as respectively tetrabasic and hexabasic sulphuric acid, and their relation to the ordinary dibasic acid may be expressed by the following formulæ—

H_2SO_4 . . . or $SO_2(HO)_2$.
H_4SO_5 or H_2SO_4,H_2O „ $SO(HO)_4$.
H_6SO_6 „ $H_2SO_4,2H_2O$ „ $S(HO)_6$.

Salts of each of these acids are known—

Hydrogen potassium sulphate . .	$HKSO_4$	Derived from H_2SO_4
Normal potassium sulphate . .	K_2SO_4	
Barium sulphate	$BaSO_4$	
Tetrabasic lead sulphate . . .	Pb_2SO_5	,, ,, H_4SO_5.
Hexabasic mercuric sulphate (Turpeth mineral) .	Hg_3SO_6	,, ,, H_6SO_6.

Most sulphates are soluble in water; those of lead, calcium, and strontium are only very sparingly soluble, whilst barium sulphate is insoluble both in water and acids. The presence of sulphuric acid or a sulphate may therefore be readily detected by the addition of a soluble barium salt, which causes the immediate precipitation of white barium sulphate, insoluble in hydrochloric acid.

PYROSULPHURIC ACID (*Nordhausen Acid; Fuming Sulphuric Acid*).

$$\text{Formula, } H_2S_2O_7 \text{ or } \left.\begin{matrix} HO{\cdot}SO_2 \\ HO{\cdot}SO_2 \end{matrix}\right\} O.$$

Modes of Formation.—(1.) This acid may be obtained by dissolving sulphur trioxide in ordinary sulphuric acid—

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

On cooling the solution to 0° the pyrosulphuric acid separates out in the form of large colourless crystals.

(2.) Pyrosulphuric acid is manufactured by the distillation of ferrous sulphate in clay retorts, mounted in series in a large "galley" furnace. The first action of heat upon crystallised ferrous sulphate (green vitriol) is to expel six molecules of water of crystallisation, leaving the salt of the composition $FeSO_4,H_2O$. When this substance is further heated it is decomposed finally into ferric oxide, with the formation of sulphur trioxide, water, and sulphur dioxide, thus—

$$2FeSO_4,H_2O = Fe_2O_3 + SO_3 + SO_2 + 2H_2O.$$

The decomposition takes place in two stages, the sulphur dioxide and water being evolved in the first part of the process with the formation of ferric sulphate, which is afterwards broken up in the manner shown in the following equation—

$$(1.)\ 6FeSO_4,H_2O = Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2 + 6H_2O.$$
$$(2.)\ Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

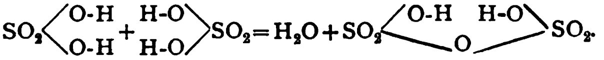
The sulphur trioxide is condensed in receivers containing either a small quantity of water or a charge of sulphuric acid.

(3.) Pyrosulphuric acid may also be obtained by decomposing sodium pyrosulphate ($Na_2S_2O_7$), either by heating it to a high temperature (see Sulphur Trioxide, page 422), or by acting upon it with sulphuric acid, thus—

$$Na_2S_2O_7 + H_2SO_4 = 2HNaSO_4 + SO_3.$$

The sulphur trioxide obtained is dissolved in sulphuric acid, as in the former methods; and the hydrogen sodium sulphate, when gently heated to about 300°, is reconverted into pyrosulphate by the loss of a molecule of water (page 422).

Properties.—Pyrosulphuric acid is a colourless, strongly fuming liquid, having a specific gravity of 1.88. When cooled, it solidifies to a crystalline mass, which melts at 35°. The compound may be regarded as consisting of one molecule of sulphuric acid *plus* a molecule of sulphur trioxide, H_2SO_4,SO_3; or, as being derived from two molecules of sulphuric acid, by the withdrawal of one molecule of water, thus—



$$SO_2\left\langle\begin{matrix}O\text{-}H\\O\text{-}H\end{matrix}\right. + \left.\begin{matrix}H\text{-}O\\H\text{-}O\end{matrix}\right\rangle SO_2 = H_2O + SO_2\left\langle\begin{matrix}O\text{-}H \qquad H\text{-}O\\O\end{matrix}\right\rangle SO_2.$$

Pyrosulphuric acid forms a stable series of salts, of which the sodium compound already mentioned is a typical example. These salts are sometimes spoken of as the *disulphates*, and are analogous to the dichromates (*q.v.*).

Two other definite compounds of sulphur trioxide and sulphuric acid are known to exist, both of which are fuming acids. The composition of these substances is expressed by the formulæ—

$$H_2SO_4,3SO_3, \text{ or } H_2S_4O_{13}; \text{ and } 3H_2SO_4,SO_3, \text{ or } H_6S_4O_{15}.$$

THIOSULPHURIC ACID.

Formula, $H_2S_2O_3$.

This acid has never been obtained in the free state, as it decomposes almost as soon as liberated from its salts into sulphur dioxide and water, with precipitation of sulphur—

$$H_2S_2O_3 = SO_2 + H_2O + S.$$

The thiosulphates, however, are stable and important salts, the sodium salt being largely used in photography under the name of *hyposulphite of soda*, or "hypo."

Modes of Formation of Thiosulphates.—(1.) These salts may be obtained by digesting flowers of sulphur with solutions of the sulphites, thus—

$$Na_2SO_3+S=Na_2S_2O_3.$$

(2.) Sodium thiosulphate is also formed when sulphur dioxide is passed into a solution of sodium sulphide. The reaction may be regarded as taking place in three steps, in which sodium sulphite and sulphuretted hydrogen are the first products. The latter compound is then acted upon by sulphur dioxide, with the precipitation of sulphur, thus—

$$SO_2+H_2O+Na_2S=Na_2SO_3+H_2S.$$
$$SO_2+2H_2S=2H_2O+3S.$$

And the sulphur reacts with the already formed sulphite, as indicated in the equation given above.

(3.) When sulphur is boiled with sodium hydroxide, or with milk of lime, mixtures of sulphides and thiosulphates are obtained in both cases—

$$6NaHO+4S=Na_2S_2O_3+2Na_2S+3H_2O.$$
$$3Ca(HO)_2+12S=CaS_2O_3+2CaS_5+3H_2O.$$

The sodium sulphide can be converted into thiosulphate by the reactions given above. Calcium pentasulphide, on exposure to air, absorbs oxygen and forms a further quantity of thiosulphate with precipitation of sulphur—

$$CaS_5+3O=3S+CaS_2O_3.$$

The thiosulphates are decomposed by most acids, with the liberation of sulphur dioxide, and precipitation of sulphur. They show a great tendency to form double salts, many of which are soluble in water; thus sodium thiosulphate, in contact with either silver chloride, bromide, or iodide, forms the soluble double sodium-silver thiosulphate, $NaAgS_2O_3$—

$$Na_2S_2O_3+AgCl=NaCl+NaAgS_2O_3.$$

The employment of sodium thiosulphate in photography, for "fixing" negatives or silver prints, depends upon this property.

Thiosulphuric acid may be regarded as being derived from sulphuric acid by the replacement of one of the (HO) or hydroxyl groups, by an equivalent of (HS) or hydrosulphyl—

$$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2. \qquad \left.\begin{matrix}HS\\HO\end{matrix}\right\}SO_2.$$

Dithionic Acid, $H_2S_2O_6$ or $\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}$.—This compound is prepared by passing a stream of sulphur dioxide through water in which manganese dioxide is suspended, whereby manganese dithionate is formed; while at the same time a portion of the salt is acted upon by manganese dioxide, and converted into manganous sulphate, thus—

$$2SO_2+MnO_2=MnS_2O_6.$$
$$MnS_2O_6+MnO_2=2MnSO_4.$$

On the addition of barium hydroxide to the solution, barium dithionate, barium sulphate, and manganous hydrate are formed—

$$MnS_2O_6+Ba(HO)_2=BaS_2O_6+Mn(HO)_2.$$

Barium dithionate, being soluble, is separated by filtration, and upon evaporation separates out in crystals of the composition $BaS_2O_6,2H_2O$.

Upon the addition of dilute sulphuric acid in amount demanded by the equation—

$$BaS_2O_6+H_2SO_4=BaSO_4+H_2S_2O_6,$$

the acid itself is obtained. The solution may be concentrated in vacuo until it reaches a specific gravity of 1.347. Further concentration results in its decomposition into sulphuric acid and sulphur dioxide—

$$H_2S_2O_6=SO_2+H_2SO_4.$$

Dithionic acid forms well-defined crystalline salts, which on heating decompose into sulphates with evolution of sulphur dioxide.

Dithionic acid was formerly called *hyposulphuric* acid, and its salts are still sometimes referred to as *hyposulphates.*

Trithionic Acid, $H_2S_3O_6$ or $\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}S$.—The potassium salt of this acid may be obtained by passing sulphur dioxide through a strong solution of potassium thiosulphate—

$$3SO_2+2K_2S_2O_3=S+2K_2S_3O_6.$$

It is also formed when a solution of potassium silver thiosulphate is boiled—

$$\begin{matrix}\left.\begin{matrix}KO\\AgS\end{matrix}\right\}SO_2\\\left.\begin{matrix}AgS\\KO\end{matrix}\right\}SO_2\end{matrix}=Ag_2S+\left.\begin{matrix}KO{\cdot}SO_2\\KO{\cdot}SO_2\end{matrix}\right\}S.$$

The sodium salt may be obtained by the addition of iodine to a mixture of sodium sulphite and thiosulphate—

$$\left.\begin{matrix}\mathrm{NaO}\\ \mathrm{NaS}\end{matrix}\right\}\mathrm{SO_2}+\mathrm{Na_2SO_3}+\mathrm{I_2}=2\mathrm{NaI}+\left.\begin{matrix}\mathrm{NaO{\cdot}SO_2}\\ \mathrm{NaO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S}.$$

The acid itself is obtained by the addition of fluosilicic acid to a solution of the potassium salt, when insoluble potassium fluosilicate is precipitated.

Both the acid itself and its salts are readily decomposed into sulphur dioxide, sulphur, and either sulphuric acid or a sulphate, thus—

$$\mathrm{K_2S_3O_6}=\mathrm{K_2SO_4}+\mathrm{SO_2}+\mathrm{S}.$$

When acted upon by sodium amalgam, sodium trithionate is converted back again into its generators, sodium sulphite and thiosulphate, thus—

$$\left.\begin{matrix}\mathrm{NaO{\cdot}SO_2}\\ \mathrm{NaO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S}+\mathrm{Na_2}=\mathrm{Na_2SO_3}+\left.\begin{matrix}\mathrm{NaO}\\ \mathrm{NaS}\end{matrix}\right\}\mathrm{SO_2}.$$

Tetrathionic Acid, $H_2S_4O_6$ or $\left.\begin{matrix}\mathrm{HO{\cdot}SO_2}\\ \mathrm{HO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S_2}$.—The sodium salt is obtained by the action of iodine upon sodium thiosulphate—

$$2\mathrm{NaS{\cdot}NaO{\cdot}SO_2}+\mathrm{I_2}=2\mathrm{NaI}+\left.\begin{matrix}\mathrm{NaO{\cdot}SO_2}\\ \mathrm{NaO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S_2}.$$

The barium salt, from which the acid itself is most readily obtained, is prepared by the gradual addition of iodine to barium thiosulphate in water—

$$2\mathrm{BaS_2O_3}+\mathrm{I_2}=\mathrm{BaI_2}+\mathrm{BaS_4O_6}.$$

The barium tetrathionate is separated by the addition of alcohol, which dissolves the iodide and excess of iodine, leaving the tetrathionate. By the addition of dilute sulphuric acid to an aqueous solution of this salt, in amount demanded by the equation—

$$\mathrm{BaS_4O_6}+\mathrm{H_2SO_4}=\mathrm{H_2S_4O_6}+\mathrm{BaSO_4},$$

a dilute aqueous solution of the acid may be obtained. The dilute acid may be boiled without decomposition; but when concentrated, it readily passes into sulphuric acid, sulphur dioxide, and sulphur.

Sodium amalgam decomposes the sodium salt into two molecules of thiosulphate, reversing the reaction by which it is produced.

Pentathionic Acid, $H_2S_5O_6$ or $\left.\begin{matrix}\mathrm{HO{\cdot}SO_2}\\ \mathrm{HO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S_3}$.—This acid is prepared by passing sulphuretted hydrogen into a strong aqueous solution of sulphur dioxide—

$$5\mathrm{SO_2}+5\mathrm{H_2S}=\mathrm{H_2S_5O_6}+5\mathrm{S}+4\mathrm{H_2O}.$$

or—

$$5\mathrm{H_2SO_3}+5\mathrm{H_2S}=\mathrm{H_2S_5O_6}+5\mathrm{S}+9\mathrm{H_2O}.$$

The solution contains, however, more or less of the other thionic acids, but as the passage of sulphuretted hydrogen is continued, these are gradually decomposed, and ultimately the pentathionic acid also, so that the final products of the action of excess of this gas will be sulphur and water—

$$H_2S_5O_6+5H_2S=6H_2O+10S.$$

The solution obtained by the first action may be concentrated by cautious evaporation in vacuo, until a specific gravity of 1.46 is obtained, when on partial saturation with potassium hydroxide and filtration, a solution is obtained which on spontaneous evaporation deposits crystals of potassium pentathionate, having the composition $K_2S_5O_6,3H_2O$. On heating, the salt splits up into potassium sulphate, sulphur dioxide, and sulphur.

OXYCHLORIDES OF SULPHUR.

Four of these compounds are known, all of which may be regarded as being derived from the oxyacids by the replacement of hydroxyl (HO) by its equivalent of chlorine.

1.	Thionyl chloride, or *Sulphurous chloride*	$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO$	corresponding oxyacid	$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO,$	sulphurous acid.
2.	Sulphuryl chloride, or *Sulphuric chloride*	$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2$	,,	,, $\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2,$	sulphuric acid.
3.	Sulphuric chlorhydrate, or *Chlorosulphonic acid*	$\left.\begin{matrix}Cl\\HO\end{matrix}\right\}SO_2$	,,	,,	
4.	Disulphuryl chloride, or *Pyrosulphuric chloride*	$\left.\begin{matrix}Cl{\cdot}SO_2\\Cl{\cdot}SO_2\end{matrix}\right\}O$	,,	$\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}O,$	pyrosulphuric acid.

Thionyl Chloride, $SOCl_2$, molecular weight=118.96, is obtained by the action of phosphorus pentachloride upon sodium sulphite—

$$SO(NaO)_2+2PCl_5=SOCl_2+2POCl_3+2NaCl.$$

It is also obtained when dry sulphur dioxide is passed over phosphorus pentachloride—

$$SO_2+PCl_5=SOCl_2+POCl_3.$$

Properties.—Thionyl chloride is a colourless and highly refractive liquid which fumes in moist air, and has a pungent unpleasant smell. It boils at 78°, and is at once decomposed by water into its corresponding oxyacid, with formation of hydrochloric acid—

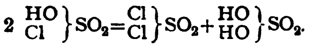
$$SOCl_2+2H_2O=H_2SO_3+HCl.$$

Sulphuryl Chloride, SO_2Cl_2; molecular weight=134.96. This compound (sometimes known as *chlorosulphuric acid*) can be obtained by the direct union of chlorine and sulphur dioxide, under the prolonged influence of bright sunlight—

$$SO_2+Cl_2=SO_2Cl_2.$$

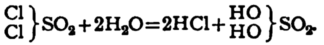
It is also formed by the action of heat upon sulphuric chlorhydrate.

This substance, on being simply heated to 180° in sealed tubes for a few hours, breaks up into sulphuryl chloride and sulphuric acid—



$$2\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2=\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2+\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

Properties.—Sulphuryl chloride is a colourless liquid, which fumes in moist air, and has a specific gravity of 1.66. It boils at 70°, and is decomposed by water, with formation of sulphuric acid and hydrochloric acid—

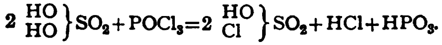


$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2+2H_2O=2HCl+\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

Sulphuric Chlorhydrate, $SO_2Cl(HO)$.—This compound is the first product of the replacement of the (HO) groups in sulphuric acid by chlorine, and is formed by the direct combination of sulphur trioxide and hydrochloric acid—

$$SO_3+HCl=HClSO_3 \text{ or } SO_2Cl(HO).$$

It may be obtained by distilling sulphuric acid with phosphorus oxychloride—

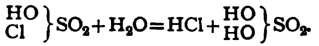


$$2\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2+POCl_3=2\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2+HCl+HPO_3.$$

Or by passing dry gaseous hydrochloric acid into melted pyrosulphuric acid—

$$H_2S_2O_7+2HCl=H_2O+2HClSO_3.$$

Properties.—Sulphuric chlorhydrate is a colourless fuming liquid, having a specific gravity of 1.76, and boiling at 149°–151°, with partial dissociation into its generators, sulphur trioxide and hydrochloric acid. In contact with water it is decomposed with considerable violence, with formation of sulphuric and hydrochloric acids—



$$\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2+H_2O=HCl+\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

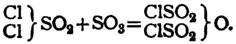
Disulphuryl Chloride (*pyrosulphuric chloride*), $\left.\begin{matrix}ClSO_2\\ClSO_2\end{matrix}\right\}O$ or $S_2O_5Cl_2$. This substance is obtained by the action of sulphur trioxide, or sulphuric chlorhydrate, upon phosphorus pentachloride—

$$2SO_3+PCl_5=POCl_3+S_2O_5Cl_2.$$
$$2SO_2Cl(HO)+PCl_5=POCl_3+2HCl+S_2O_5Cl_2.$$

It is also produced by the action of sulphur trioxide upon sulphur dichloride—

$$5SO_3+S_2Cl_2=S_2O_5Cl_2+5SO_2.$$

Or by the action of sulphur trioxide upon sulphuric chloride—



$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2+SO_3=\left.\begin{matrix}ClSO_2\\ClSO_2\end{matrix}\right\}O.$$

Properties.—Pyrosulphuric chloride is a heavy, oily, fuming liquid, resembling pyrosulphuric acid in appearance. It has a specific gravity of 1.819, and boils at 146°. When mixed with water it slowly decomposes into sulphuric and hydrochloric acids, showing a marked difference in this respect from sulphuric chlorhydrate—

$$S_2O_5Cl_2+3H_2O=2H_2SO_4+2HCl.$$

COMPOUNDS OF SULPHUR WITH FLUORINE.

Perfluoride of Sulphur, SF_6.—This compound has been recently obtained (Moissan) by passing fluorine over sulphur.

Properties.—Sulphur perfluoride is a colourless inodorous gas, very soluble in water, and incombustible in air. It is a comparatively inactive compound.

Thionyl Fluoride, SOF_2, is obtained by the action of fluorine upon thionyl chloride; also by the action of arsenic trifluoride upon thionyl chloride—

$$2AsF_3+3SOCl_2=3SOF_2+AsCl_3.$$

Properties.—Thionyl fluoride is a colourless gas which fumes strongly in moist air. It is immediately decomposed by water—

$$SOF_2+H_2O=2HF+SO_2.$$

CARBON DISULPHIDE.

Formula, CS_2. Molecular weight=76.12. Vapour density=38.06.

History.—This compound was accidentally produced by Lampadius (1796) when heating a mixture of charcoal and pyrites.

Mode of Formation.—Carbon disulphide is prepared by passing the vapour of sulphur over red-hot charcoal, when the two elements unite and form the volatile product, which is condensed in vessels surrounded with cold water—

$$C+S_2=CS_2.$$

The product is always contaminated with free sulphur, which volatilises, and is also accompanied by considerable quantities of sulphuretted hydrogen, formed by the action of sulphur upon the hydrogen contained in the charcoal.

When carbon disulphide is prepared on a manufacturing scale, the charcoal is heated in a vertical cast-iron or earthenware retort, C (Fig. 117), having an elliptical section, and provided with three openings. The retort is built into a suitable furnace, whereby it can be uniformly heated to redness. A quantity of sulphur, contained in the pot S, kept liquid by the heat of the furnace, is allowed to enter at intervals through the pipe B. As the vapour comes in contact with the red-hot charcoal, combination ensues, and the carbon disulphide escapes through the pipe D, which is inclined to the retort so as to allow condensed sulphur to run back. Sulphur which escapes condensation in this pipe, collects, for the most part, in the vessel E, which is closed by water seals, as seen in the figure. The volatile compounds are then passed through a Liebig's condenser about 30 ft. long, and the crude disulphide so condensed is collected in a receiver. Any vapour of carbon disulphide which is carried on by the sulphuretted hydrogen is absorbed by passing the gas through a scrubber containing oil; and finally the sulphuretted hydrogen is absorbed in a lime purifier, similar to those employed for the purification of coal gas. The ashes are withdrawn from the retort through the wide tube B; and the fresh charcoal is introduced through the opening A. In order to prevent the escape of the unpleasant and injurious vapours from A during the addition of fresh charcoal, the opening A′ is put into communication with the chimney of the furnace. The sulphur which flows back into the retort from D is conveyed, by means of the pipe *f*, nearly to the bottom of the mass of heated charcoal, so that its vapour shall once more be made to pass over the carbon.

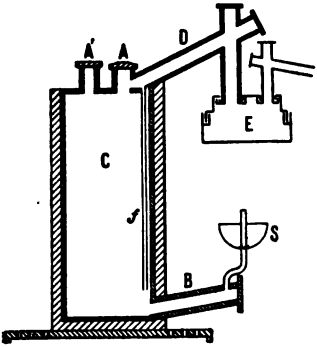


FIG. 117.

At the present day, since the application of electrical heating to manufacturing processes, the mixture, instead of being heated from the *outside* by fuel, is heated *inside* in vessels of modified form by means of the electric arc.

The crude product is purified by distillation and subsequent agitation with mercury.

Properties.—Carbon disulphide is a colourless, mobile, and highly refracting liquid. When perfectly pure it possesses a sweetish, and not unpleasant, ethereal smell, but as usually met with the odour is decidedly fœtid.

Its specific gravity at 0° is 1.292, and it boils at 46°. The vapour of carbon disulphide has a very low igniting-point (see page 329). It burns with a blue flame, which, when fed with oxygen, emits a dazzling blue light. When carbon disulphide vapour is mixed with three times its volume of oxygen, and a light applied, the mixture explodes with violence; the products of the combustion being carbon dioxide and sulphur dioxide—

$$CS_2+3O_2=CO_2+2SO_2.$$

The vapour of carbon disulphide, when constantly inhaled in small quantities, has an injurious effect upon the health, and if breathed in large quantities is a powerful poison.

When heated to a bright red heat, carbon disulphide vapour is decomposed into its constituent elements: on this account, in the manufacture of this compound, care is taken that the temperature does not rise too high.

The vapour of carbon disulphide is decomposed by potassium, which, when heated, burns in the vapour, forming potassium sulphide, and liberating carbon—

$$CS_2+2K_2=C+2K_2S.$$

When passed over heated slaked lime, carbon disulphide vapour is converted into carbon dioxide and sulphuretted hydrogen—

$$CS_2+2CaH_2O_2=2CaO+CO_2+2H_2S.$$

This reaction is made use of for converting the carbon disulphide, which is always present in coal gas, into the two easily removed substances, carbon dioxide and sulphuretted hydrogen.

When a mixture of carbon disulphide vapour and sulphuretted hydrogen is passed over heated copper, marsh gas is formed—

$$4Cu+CS_2+2H_2S=CH_4+4CuS.$$

Carbon disulphide is soluble to a minute extent in water; 1 volume of water dissolves .001 volume of this liquid, and the solution possesses the taste and the smell of the disulphide. It mixes in all proportions with alcohol, ether, the hydrocarbons of the benzene family, and most essential oils. It also dissolves sulphur, phosphorus, iodine, bromine, caoutchouc, and most fats; and is largely used in the arts, both as a solvent for caoutchouc and in extracting essential oils, spices, and perfumes.

Thiocarbonic Acid.—Carbon disulphide is the sulphur analogue of carbon dioxide, CS_2; CO_2. Like the oxygen compound, It forms a feeble acid, which has received the name thiocarbonic acid, H_2CS_3 ; carbonic acid, H_2CO_3.

The thiocarbonates are produced by reactions analogous to those by which carbonates are formed. Thus, when carbon disulphide is brought into contact with potassium sulphide, potassium thiocarbonate is obtained—

$$CS_2 + K_2S = K_2CS_3.$$

Thiocarbonates are likewise formed by the action of carbon disulphide upon metallic hydroxides—

$$3CS_2 + 6KHO = 2K_2CS_3 + K_2CO_3 + 3H_2O.$$

The acid itself is obtained as a yellow oil, having an unpleasant odour by the decomposition of a thiocarbonate by dilute hydrochloric acid.

A large number of compounds are known in which divalent sulphur replaces oxygen, and which therefore stand in the same relation to the oxygen compounds as thiocarbonic acid stands to carbonic acid ; for example—

$$\text{Thiocarbamic acid, } CS_2{,}NH_3, \text{ or } \left.\begin{matrix} NH_2 \\ HS \end{matrix}\right\} CS \text{ ;}$$

$$\text{Carbamic acid, } CO_2{,}NH_3, \text{ or } \left.\begin{matrix} NH_2 \\ HO \end{matrix}\right\} CO.$$

Other Compounds of Carbon and Sulphur.—When carbon disulphide is exposed to the influence of light, there is gradually formed upon the glass vessel containing it a brown deposit, which is believed to be carbon monosulphide, CS; the sulphur analogue of carbon monoxide. When electric sparks from carbon poles are passed through the vapour of carbon disulphide, or when the electric arc is produced in the vapour, an offensive smelling liquid is obtained, which exerts a most irritating and tear-producing effect upon the eyes. This liquid has been shown to have the composition C_3S_2.*

SELENIUM.

Symbol, Se. Atomic weight = 79.1. Molecular weight = 158.2.

History.—This element was discovered by Berzelius (1817), who gave it the name selenium (signifying the moon) on account of its close analogy with the previously discovered element tellurium (signifying the earth).

Occurrence.—Selenium is occasionally met with associated with native sulphur, probably as a selenide of sulphur. In a few minerals of considerable

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* Von Lengyel, 1894.

rarity, selenium is met with in the form of selenides of such metals as mercury, lead, silver. It occurs in very small quantities in a large number of metallic sulphides.

Modes of Formation.—(1.) When pyrites containing selenium is employed in the manufacture of sulphuric acid, the selenium is oxidised by the atmospheric oxygen into selenium dioxide, which is carried forward with the sulphur dioxide. Selenium dioxide, being a solid substance, is partly deposited in the flues, and in the Glover tower, and partly carried forward into the chambers, where it forms a red-coloured deposit. To obtain the selenium, either the flue dust or the chamber deposit is first boiled with dilute sulphuric acid, and either nitric acid or potassium chlorate added, in order to oxidise it completely into selenic acid, H_2SeO_4. The solution is then boiled with strong hydrochloric acid, whereby it is reduced to selenious acid, H_2SeO_3, when a stream of sulphur dioxide is passed through it which precipitates the selenium as a red powder—

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4.$$

(2.) A second method for the preparation of selenium from the chamber deposit consists in digesting the substance with potassium cyanide, whereby it is converted into soluble potassium selenocyanide, SeK(CN). On the addition of hydrochloric acid to this solution, the element is precipitated as a red amorphous powder, and hydrocyanic acid and potassium chloride go into solution—

$$SeK(CN) + HCl = Se + KCl + H(CN).$$

Properties.—Selenium is known in various allotropic modifications.

1. *Soluble in carbon disulphide.*—*a.* Brick-red amorphous powder, obtained by precipitation with acids, or reduction of selenious acid, in the cold, by sulphur dioxide.

β. Black crystalline powder, obtained by reduction of hot selenious acid by sulphur dioxide.

γ. Dark red translucent monoclinic crystals, specific gravity 4.5, deposited from solution in carbon disulphide.

δ. Black, shining, brittle amorphous mass, having a conchoidal fracture, and a specific gravity of 4.3, obtained by rapidly cooling melted selenium.

2. *Insoluble in carbon disulphide.*—Black, metallic-looking crystalline mass, having a granular fracture. Obtained by quickly cooling melted selenium to 210° and keeping it for some time at that temperature, when the mass solidifies with rise of temperature to 217°. This insoluble variety, sometimes called *metallic* selenium, is also formed as a deposit of minute black crystals, when concentrated solutions of sodium or potassium selenide are exposed to the air.

This modification has a specific gravity of 4.5, and melts at 217°.

Selenium boils at 680°, forming a dark-red vapour which condenses in the form of *flowers of selenium*, having a scarlet-red colour.

At high temperatures the vapour of selenium, like that of sulphur, becomes a true gas; thus at 1420°, the vapour-density is found to be 81.5, approaching very closely to the normal density demanded by the molecule Se_2.

"Metallic" selenium conducts electricity, and the element exhibits the remarkable property of having its conductivity increased by light; the conductivity of selenium when exposed to diffused daylight being about twice as great as when in the dark. This alteration in the electrical resistance with varying intensities of light, is a property of selenium that was made use of in the construction of an instrument known as the photophone, but it has not as yet been put to any practical use. When selenium is heated in the air, it burns with a blue flame, with the formation of selenium dioxide, and at the same time emits a powerful and characteristic smell resembling rotten horse-radish.

When selenium is heated in a tube filled with an indifferent gas, it sublimes in the form of a red deposit; but when heated in hydrogen, the sublimate is in the form of black shining crystals. The formation of these crystals is due to the fact that selenium combines with the hydrogen, and the hydrogen selenide is again decomposed by the heat.

Hydrogen Selenide (*selenuretted hydrogen*), H_2Se; molecular weight=81.12. Hydrogen selenide is formed when selenium is heated in hydrogen.

This compound is also obtained by the action of dilute hydrochloric or sulphuric acid upon either potassium selenide or ferrous selenide—

$$FeSe + H_2SO_4 = FeSO_4 + H_2Se.$$

Properties.—Hydrogen selenide is a colourless gas, strongly resembling sulphuretted hydrogen, both in its smell and in its chemical behaviour. It is readily soluble in water, and when passed through metallic solutions precipitates insoluble selenides of most of the heavy metals. Hydrogen selenide burns with a blue flame, with the production of water and selenium dioxide. Its smell, although resembling that of its sulphur analogue, is more unpleasant, and its effects upon the system are more persistent and injurious. A single small bubble inhaled through the nostril produces temporary paralysis of the olfactory nerves, accompanied by inflammation of the mucous membrane.

No compound of selenium corresponding to hydrogen disulphide is known.

COMPOUNDS WITH HALOGENS.

Diselenium Dichloride, Se_2Cl_2, is obtained by passing chlorine over selenium, or by passing gaseous hydrochloric acid through a solution of selenium in nitric acid.

Properties.—Selenium chloride is a brown oily liquid, in which selenium itself is readily soluble, and from which the element is deposited in the form which is insoluble in carbon disulphide. It is slowly decomposed by water, thus—

$$2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl.$$

Corresponding bromine and iodine compounds are known, Se_2Br_2, and Se_2I_2.

Selenium Tetrachloride, $SeCl_4$, is prepared either by the action of chlorine upon selenium chloride—

$$Se_2Cl_2 + 3Cl_2 = 2SeCl_4,$$

or by heating a mixture of selenium dioxide and phosphorus pentachloride—

$$3SeO_2 + 3PCl_5 = 3SeCl_4 + P_2O_5 + POCl_3.$$

Properties.—Selenium tetrachloride is a white, crystalline, volatile compound; which may be sublimed without decomposition and without fusion.

When the vapour is heated above 200° it begins to dissociate into selenium and chlorine. It dissolves in water, with decomposition into hydrochloric and selenious acids—

$$SeCl_4 + 3H_2O = 4HCl + H_2SeO_3.$$

Corresponding bromine and iodine compounds are known, $SeBr_4$ and SeI_4.

OXIDES AND OXYACIDS OF SELENIUM.

Only one oxide of selenium is known, namely, selenium dioxide, SeO_2, although a second oxide of unknown composition is believed to exist, and to constitute the peculiar smelling substance which is always formed when selenium is burnt in the air.

Selenium Dioxide is prepared by burning selenium in a stream of oxygen in a glass tube; the element burns in the gas with a blue flame, and the oxide condenses upon the distant portions of the tube, as a white crystalline deposit.

Properties.—Selenium dioxide crystallises in long white prisms, which when heated readily sublime without passing through the state of liquidity. It dissolves in water and gives rise to selenious acid.

The following oxyacids of selenium are known—

Selenious acid, H_2SeO_3, corresponding to sulphurous acid, H_2SO_3.
Selenic acid, H_2SeO_4, corresponding to sulphuric acid, H_2SO_4.
Selenosulphuric acid $\left.\begin{array}{l}HO\\HSe\end{array}\right\}SO_2$, corresponding to $\left\{\right.$ thiosulphuric acid, $\left.\begin{array}{l}HO\\HS\end{array}\right\}SO_2$.

Selenious Acid, H_2SeO_3, is obtained as a white crystalline compound, when the dioxide is dissolved in hot water, and the solution allowed to cool. The acid is dibasic, and forms both acid and normal selenites, corresponding to the sulphites: it also forms a series of so-called *superacid salts*, containing a molecule of the acid salt combined with a molecule of acid, thus—

$$HKSeO_3, H_2SeO_3.$$

Selenic Acid, H_2SeO_4.—This acid is best prepared by the addition of bromine to silver selenite suspended in water, when insoluble silver bromide is formed and selenic acid is left in solution—

$$Ag_2SeO_3 + H_2O + Br_2 = 2AgBr + H_2SeO_4.$$

The solution may be evaporated by heating until it contains 94 per cent. of selenic acid, and still further evaporated in vacuo until it reaches 97.4 per cent., when its specific gravity is 2.627. When heated to 280° it decomposes into selenium dioxide, water, and selenium.

Properties.—Selenic acid in its most concentrated condition is a colourless, strongly-acid liquid, which mixes with water with the development of considerable heat. It dissolves iron and zinc with evolution of hydrogen; and when heated dissolves copper with formation of selenious acid.

The selenates closely resemble the sulphates. Barium selenate, like the sulphate, is quite insoluble in water, but differs from that compound in being converted by boiling hydrochloric acid into barium selenite, which is soluble.

Selenium also forms a compound with oxygen and chlorine, selenium oxychloride, or selenyl chloride, $SeOCl_2$, corresponding with thionyl chloride, $SOCl_2$.

TELLURIUM.

Symbol, Te. Atomic weight* = 127.6.

Occurrence.—In the free state small quantities of this element have been found as crystals, consisting of almost pure tellurium. In combination it is met with in a few rare minerals, such as *tellurite* (TeO_2), and, more commonly, *tetradymite* (Bi_2Te_3). Some specimens of pyrites contain small quantities of this element, hence it is found in the deposit from the vitriol chambers, from which selenium is obtained.

Mode of Formation.—Tellurium is obtained from bismuth telluride, Bi_2Te_3, by fusion with an intimate mixture of sodium carbonate and carbon. The mass on treatment with water yields a solution containing a mixture of sodium telluride and sodium sulphide, which on exposure to the air deposits tellurium as a grey powder. The element is purified by distillation in a stream of hydrogen.

Properties.—Tellurium is a bluish-white, silver-like solid, possessing metallic lustre. It conducts heat and electricity, although badly, and is very brittle. Its specific gravity is 6.26, and it melts at 452°. When melted tellurium is slowly cooled, it forms rhombohedral crystals. When heated in the air it burns with a blue flame, and forms tellurium dioxide, TeO_2. When heated in a sealed tube with hydrogen, tellurium sublimes in the form of brilliant prismatic crystals.

Hydrogen Telluride (*telluretted hydrogen*), H_2Te.—When tellurium is heated in hydrogen the elements combine, forming hydrogen telluride, which exhibits the same phenomenon as is shown by hydrogen selenide of being decomposed by heat, and depositing the element as a crystalline sublimate.

Hydrogen telluride is obtained by the action of hydrochloric acid upon zinc telluride—

$$ZnTe + 2HCl = ZnCl_2 + H_2Te.$$

Properties.—Hydrogen telluride is a most offensive smelling and highly poisonous gas. It behaves like sulphuretted hydrogen in precipitating metals from solutions. It is soluble in water, and the solution gradually absorbs oxygen and deposits tellurium.

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* Various numbers have been obtained by different observers for the atomic weight of tellurium. Some of these numbers are higher than the atomic weight of iodine, which would make it impossible to give to tellurium a position between antimony (atomic weight = 120) and iodine (atomic weight = 126.97) as demanded by the periodic law. Brauner, who has spent many years investigating this point, considers that hitherto *pure* tellurium has never been obtained. The most recent determinations give the number 127.6.

COMPOUNDS WITH THE HALOGENS.

Two chlorides of tellurium are known, namely, tellurium dichloride, $TeCl_2$, and tellurium tetrachloride, $TeCl_4$. It will be noticed that the composition of the dichloride is not analogous with the lower chloride of either selenium (Se_2Cl_2) or sulphur (S_2Cl_2).

Two bromides, $TeBr_2$ and $TeBr_4$, and corresponding iodides are known.

OXIDES AND OXYACIDS OF TELLURIUM.

Two oxides of tellurium are known with certainty, namely, tellurium dioxide, TeO_2, and tellurium trioxide, TeO_3, which give rise respectively to the two acids, tellurous acid, H_2TeO_3, and telluric acid, H_2TeO_4.

Tellurous Acid is obtained by pouring a solution of tellurium in nitric acid into an excess of water. The acid is precipitated as a white amorphous powder. When strongly heated it is converted into the dioxide and water.

Tellurous acid, like sulphurous acid, is dibasic, and gives rise to both acid and normal salts: thus, with potassium it forms hydrogen potassium tellurite, $HKTeO_3$, and dipotassium tellurite, K_2TeO_3. It also forms superacid salts such as—

Quadracid potassium tellurite . . .	$HKTeO_3,H_2TeO_3$.
Potassium tetratellurite	$K_2TeO_3,3TeO_2$.

Telluric Acid is prepared by fusing either tellurium or tellurium dioxide with a mixture of potassium nitrate and carbonate—

$$Te + K_2CO_3 + 2KNO_3 = 2K_2TeO_4 + N_2 + CO.$$

The fused mass, after solution in water, is mixed with a solution of barium chloride, which precipitates barium tellurate; this is then decomposed by the addition of the exact amount of sulphuric acid, and after filtration the clear solution deposits crystals of telluric acid, $H_2TeO_4,2H_2O$. When these crystals are heated to 160° the water is expelled, and the anhydrous acid in the form of a white powder is left. On strongly heating, telluric acid decomposes into water and tellurium trioxide, which at a higher temperature splits up into the dioxide and oxygen.

Like tellurous acid, telluric acid forms not only normal and acid salts, but a number of more complex superacid salts—

Normal potassium tellurate . . .	$K_2TeO_4,5H_2O$.
Hydrogen potassium tellurate . . .	$HKTeO_4$.
Quadracid potassium tellurate . . .	$K_2TeO_4,H_2TeO_4,3H_2O$.
Potassium tetratellurate	$K_2TeO_4,3H_2TeO_4,H_2O$.

CHAPTER III

THE ELEMENTS OF GROUP V. (FAMILY B.)

Nitrogen, N	14.04
Phosphorus, P	31.0
Arsenic, As	75.0
Antimony, Sb	120
Bismuth, Bi	208.5

IN this family of elements we have a gradual transition from the non-metals to the metals. Nitrogen and phosphorus may be considered as typical non-metallic elements, both as regards their physical and chemical properties. The third member, arsenic, begins to exhibit metalline properties; its specific gravity is more than three times as high as that of phosphorus, and it possesses considerable metallic lustre; arsenic is called a *metalloid* on this account. Antimony is still more metallic in its character, possessing most of the physical attributes of a true metal, while in bismuth all non-metallic properties cease altogether to exist.

All these elements form more than one compound with oxygen, of which the following may be compared—

N_2O_3 ;	$(P_2O_3)_2$;	$(As_2O_3)_2$;	Sb_2O_3 ;	Bi_2O_3.
N_2O_4 ;	P_2O_4 ;	—	Sb_2O_4 ;	Bi_2O_4.
N_2O_5 ;	P_2O_5 ;	As_2O_5 ;	Sb_2O_5 ;	Bi_2O_5.

The oxides (which in the case of nitrogen and phosphorus are strongly acidic in their nature, combining with water to form acids) gradually become less and less acidic and more basic as the series is traversed.

Thus, nitrogen pentoxide, N_2O_5, unites violently with water to form nitric acid, which with bases yields nitrates. Antimony pentoxide is insoluble in water, and no antimonic acid has been isolated, although its salts, the antimonates, are known. The oxides of antimony, on the other hand, begin to exhibit basic properties and unite with acids, forming salts in which the antimony functions as the base.

In the case of the last element the acidic nature of the oxides is entirely lost; no bismuth compounds being known corresponding to antimonates or arsenates, while these oxides unite with acids in the capacity of bases, giving rise to bismuth salts.

Four of the elements of this group unite with hydrogen, forming similarly constituted compounds, NH_3, PH_3, AsH_3, SbH_3.

The stability of these compounds gradually decreases as we pass from nitrogen to antimony. Antimony hydride has never been obtained free from other gases, while no similar bismuth compound is known. Ammonia is alkaline and strongly basic, and unites readily with acids to form ammonium salts. Phosphorus hydride has no alkaline character, and is only feebly basic. It combines, however, with the halogen acids to form phosphonium chloride, bromide, and iodide, PH_4Cl, PH_4Br, PH_4I, analogous to ammonium chloride, bromide, and iodide. The hydrides of arsenic and antimony exhibit no basic character. All the elements of this group unite with chlorine, giving rise to the compounds—

$$NCl_3,\ PCl_3,\ AsCl_3,\ SbCl_3,\ BiCl_3,$$

which also exhibit a gradation in their properties; thus, nitrogen trichloride is an extremely unstable liquid, exploding with extraordinary violence upon very slight causes, while the analogous bismuth compound is a perfectly stable solid.

The boiling-points of these compounds show a gradual increase with the increasing atomic weight of the element; thus, nitrogen chloride boils at 71°, phosphorus trichloride at 78°, arsenic trichloride at 130.2°, and antimony trichloride at 200°.

The elements arsenic, antimony, and bismuth are isomorphous, and their corresponding compounds are also isomorphous.

The first member of this family, namely, nitrogen, has been already treated in Part II. as one of the four typical elements studied in that section of the book. It occupies a position in relation to the other members of the family very similar to that of oxygen towards sulphur, selenium, and tellurium.

PHOSPHORUS.

Symbol, P. Atomic weight = 31.0. Vapour density = 62.0.
Molecular weight = 124.0.

History.—Phosphorus was first discovered by the alchemist Brand of Hamburg (1669), who obtained it by distilling a mixture of sand with urine which had been evaporated to a thick syrup. The process, however, was kept secret. Robert Boyle (1680) discovered the process of obtaining this element, but the method was not published till after his death. Until the year 1771, when Scheele published a method by which phosphorus could be obtained from bone ash, this element was looked upon as a rare chemical curiosity. The name *phosphorus* was not first coined for this element: it had been in previous use to denote various substances known at that time, which had the property of glowing in the dark. To distinguish the element it was called *Brand's phosphorus*, or *English phosphorus.*

Occurrence.—Phosphorus is not found in nature in the free state.* In combination with oxygen and metals, as phosphates, it is very widely distributed, especially as calcium phosphate. The following are some of the commonest natural phosphates—

Sombrerite, or estramadurite .	$Ca_3(PO_4)_2$.
Apatite	$3Ca_3(PO_4)_2,CaCl_2$.
Wavellite	$2Al_2(PO_4)_2,Al_2(HO)_6,9H_2O$.

Calcium phosphate is present in all fertile soils, being derived from the disintegration of rocks: the presence of phosphates in soil has been shown to be essential to the growth of plants. From the vegetable it passes into the animal kingdom, where it is chiefly present in the urine, brain, and bones. Bones contain about 60 per cent. of calcium phosphate, to which they entirely owe their rigidity.

Mode of Formation.—*Manufacture.* The chief source of phosphorus is bone ash, a material obtained by burning bones, and which consists of nearly pure calcium phosphate, $Ca_3(PO_4)_2$. Other varieties of calcium phosphate, such as sombrerite and apatite, are also employed, as well as phosphates of other metals, such as the Redonda phosphates, which consist of phosphates of iron and alumina. The bone ash, in fine powder, is first decomposed by means of sulphuric acid, specific gravity 1.5 to 1.6. This operation is performed in large circular wooden vessels, resembling a brewer's "mash tun," provided with an agitator, and into which high pressure steam can be driven. Finely-ground bone ash and sulphuric acid, in charges of a few cwts. at a time, are alternately stirred into the decomposer, until from four to five tons of

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* Farrington (*Am. Jour. Science*, vol. xv., 1903) records having discovered small quantities of free phosphorus enclosed, or occluded in a meteorite.

phosphate have been introduced, with sufficient acid to convert the *whole* of the lime into calcium sulphate, according to the equation—

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4.$$

The contents of the decomposer are next run out into filtering tanks, and the phosphoric acid is then concentrated to a syrup, in large lead-lined pans through which steam-coils pass, the liquor being constantly agitated by a mechanical stirrer.

The concentrated liquor is next mixed, either with sawdust, or with coarsely-ground charcoal, or coke, and the mixture completely dried by being heated in a cast-iron pot, or in a muffle, to a dull red heat. During this process the tribasic phosphoric acid (or orthophosphoric acid), H_3PO_4, is converted by loss of water into metaphosphoric acid, HPO_3—

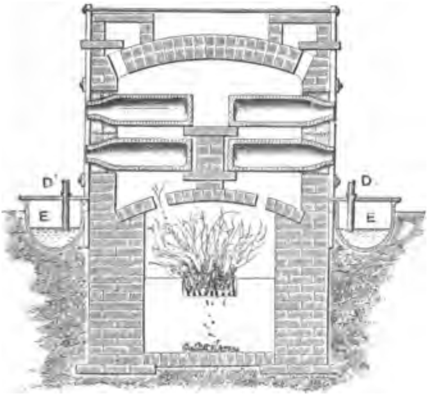

FIG. 118.

$$H_3PO_4=H_2O+HPO_3.$$

The charred mixture is then distilled in bottle-shaped retorts of Stourbridge clay, about 3 feet long, and having an internal diameter of 8 inches. A number of these retorts, usually twenty-four, are arranged in two tiers, in a galley furnace, as seen in section in Fig. 118. The empty retorts are first gradually raised to a bright red heat, and a charge of the mixture is then quickly introduced. Bent pieces of 2-inch malleable iron pipe are then luted into the mouths of the retorts connecting them with the pipes, D D′. These pipes dip into troughs of water, E E′, which run along the entire length of the furnace, and in which the phosphorus condenses. The temperature of the furnace is then raised to a white heat, when decomposition of the metaphosphoric acid commences, and phosphorus begins to distil over. The process is continued for about sixteen hours. The change that goes on is mainly represented by the following equation—

$$4HPO_3 + 12C = 12CO + 2H_2 + 4P.$$

The crude product, which is usually dark red or black in appearance, is first melted under hot water and thoroughly stirred, in order to allow the greater part of the rougher suspended matters to rise to the surface. The mass is then allowed to resolidify. The exact processes by which phosphorus is further purified on a manufacturing scale are guarded as trade secrets ; one method that has been in use consists in treating the phosphorus while melted under water with a mixture of potassium dichromate and sulphuric acid, whereby some of the impurities are oxidised and others are caused

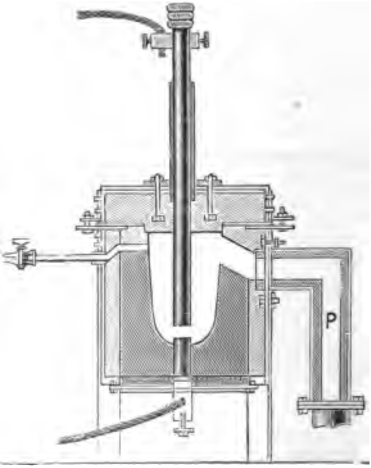

FIG. 119.

to rise to the surface as a scum, leaving the phosphorus as a clear liquid beneath.

Since the advent of the electric furnace, phosphorus is now being manufactured direct from calcium phosphate by a process which threatens to entirely supersede the method of distillation already described. The calcium phosphate is mixed with carbon and simply heated in the electric furnace. At the high temperature of the electric arc the calcium phosphate is decomposed, the calcium uniting with the carbon to form calcium carbide, while the phosphorus in the state of vapour escapes along with carbon monoxide by the pipe P (Fig. 119), and is condensed in suitable condensers—

$$Ca_3(PO_4)_2 + 14C = 3CaC_2 + 2P + 8CO.$$

The molten calcium carbide is tapped off from the furnace from time to time as fresh charges of phosphate and carbon are introduced.

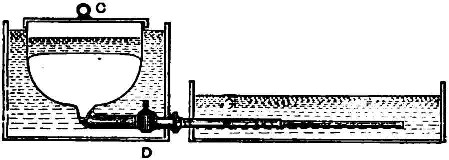

FIG. 120.

Phosphorus usually comes into commerce either in the form of wedges or as sticks. The operation of casting the phosphorus into sticks is performed beneath water. A quantity of phosphorus beneath a shallow layer of water is placed in the vessel C (Fig. 120), which is contained in a tank of water through which a steam-coil passes. Connected to the phosphorus reservoir is a glass tube, G, which passes into a second shallow tank of cold water. On opening the cock D, the liquid phosphorus flows into the cold glass tube where it congeals, and it may then be drawn through as a continuous rod of phosphorus if care be taken not to draw it out faster than it solidifies. It is the custom to adopt a uniform length and thickness of stick, namely, 7½ inches long and ½ inch diameter. Nine such sticks weigh 1 lb.

Properties.—When freshly prepared and kept in the dark, phosphorus is a translucent, almost colourless, wax-like solid. Even in the dark it soon loses its transparency and becomes coated with an opaque white film; while if exposed to the light the film that forms becomes first yellow, then brown, and in time the phosphorus assumes a red and even a black colour throughout its entire mass. Its specific gravity at 16° is 1.82. At 0° phosphorus becomes moderately brittle, and a stick of it may be readily snapped, when its crystalline character will be seen. At 15° it becomes soft, and may be cut with a knife like wax. Phosphorus melts under water at 43.3°, and the liquid exhibits the property of suspended solidification. If the melted material, which has been cooled below its solidifying point, be touched with a fragment of phosphorus upon the end of a capillary glass tube, the mass instantly congeals with rise of temperature.*

Phosphorus contained in a closed vessel without water melts at as low a temperature as 30°,† and when heated in air to 34° it takes fire. At a temperature of 269° phosphorus boils and forms a colourless vapour.

Phosphorus is volatile at ordinary temperatures: if a small quantity of phosphorus be sealed in a vacuous tube, and the tube be placed in the dark, the phosphorus will slowly vaporise; and if one end of the tube be kept slightly cooler than the rest, the phosphorus will sublime upon that part in the form of brilliant, colourless, and highly refracting rhombic crystals, which retain their beauty as long as they are kept in the dark. The density of the vapour of phosphorus is 62.0, giving a molecular weight of 124.0, which is four times the atomic weight, showing that the molecule of phosphorus contains four atoms. Even at temperatures as high as 1040° these tetratomic molecules are stable, but it has been shown that at high temperatures dissociation begins to take place.

On account of its ready inflammability, phosphorus is always preserved under water, which exerts practically no solvent action upon it. It is extremely soluble in carbon disulphide, 1 part of this liquid dissolving 9.26 parts of phosphorus. On evaporation, the element is deposited in the form of colourless crystals. Phosphorus is also soluble, but to a less extent, in chloroform, benzene, turpentine, alcohol, olive oil, and many other solvents. A solution of phosphorus in carbon disulphide, when allowed to evaporate upon a piece of blotting-paper, leaves the element in so finely divided a condition, that its rapid oxidation almost immediately raises the

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* See "Chemical Lecture Experiments," new ed., Nos. 528, 529.

† Readman.

temperature to the ignition point of the phosphorus, when it takes fire.

On exposure to moist air in the dark, phosphorus appears faintly luminous, emitting a pale greenish-white light, and at the same time evolving white fumes which possess an unpleasant, garlic-like smell, and are poisonous. These fumes consist mainly of phosphorus oxide, P_4O_6, and the glowing of the phosphorus is the result of its oxidation; phosphorus does not glow when placed in an inert gas which is perfectly free from admixed oxygen, although the presence of very small traces of free oxygen in such a gas is sufficient to cause the phosphorescence. At a few degrees below 0°, phosphorus ceases to glow in the air. Although the glowing is due to oxidation, phosphorus does not appear luminous in pure oxygen at temperatures below about 15°. If, therefore, a stick of phosphorus which is glowing in the air, be immersed in a jar of oxygen, its phosphorescence is at once stopped. If, however, the oxygen be slightly rarefied, the phosphorus again becomes luminous. Similarly, the phosphorescence that is exhibited in air is stopped if the air be compressed.* The glow of phosphorus is believed to be associated with the formation of ozone, for the presence in the air of traces of such gases and vapours as ethylene, turpentine, or ether, which are known to possess the power of destroying ozone, at once stops the glowing of a stick of phosphorus.

Phosphorus is incapable of uniting with oxygen if the gas be perfectly pure and free from aqueous vapour. It has been shown that in oxygen which has been dried by prolonged exposure to the desiccating action of phosphorus pentoxide, phosphorus may not only be melted, but even distilled, without any combination with the oxygen taking place.

If water, beneath which is a small quantity of melted phosphorus, be boiled, the phosphorus vaporises with the steam, and renders the steam luminous: use is made of this property, as a means of detecting free phosphorus, in toxicological analysis.

Phosphorus is a powerfully poisonous substance; in large doses it causes death in a few hours, in smaller quantities it produces stomachic pains and sickness, usually ending in convulsion. Persons constantly exposed to the vapours arising from the handling of phosphorus, either in its manufacture or in the manufacture

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* "Chemical Lecture Experiments," new ed., Nos. 530 to 534.

of matches, are very liable to suffer from caries of the bones of the jaw and nose; it is believed that this injurious effect is caused by the white fumes which are the product of oxidation, and not by the actual vapour of phosphorus.

Red Phosphorus.—When phosphorus is heated to a temperature between 240° and 250°, out of contact with air, it passes into an allotropic modification. The same transformation takes place when phosphorus is heated to 200° with an extremely small proportion of iodine.

Red phosphorus is manufactured by heating ordinary phosphorus in a cast-iron pot, provided with a cover, through which passes a short open pipe, D (Fig. 121). The pot is carefully and uniformly heated to between 240° and 250°, as indicated by the thermometers C C′, which are encased in metal tubes, to prevent the phosphorus from attacking the glass. A small quantity of the phosphorus becomes oxidised by the air within the vessel, but after this atmospheric oxygen is used up, no further oxidation takes place. If the temperature be allowed to rise above 260°, the red phosphorus is

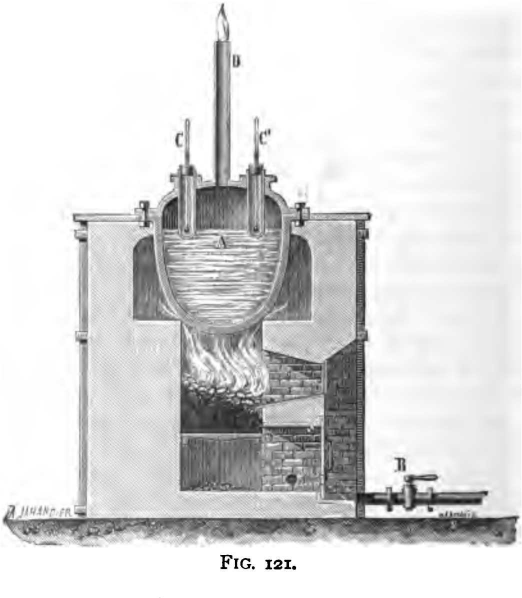

FIG. 121.

reconverted into the ordinary modification, and with the evolution of so much heat, that unless the open tube be provided, as a safety-valve, the iron vessel is liable to burst. The material that is obtained at the end of the operation is in the form of hard, solid lumps, which still contain a certain amount of the unchanged phosphorus mixed with them. It is first ground to powder beneath water, and then boiled with a solution of sodium hydroxide (caustic soda), to remove the ordinary phosphorus, and finally washed and dried.

Properties.—Red phosphorus, as usually sent into commerce, is a chocolate-red powder, having a specific gravity of 2.25. It is not luminous in the dark, and has no taste or smell. It is not poisonous, and when taken into the system is excreted unchanged. It is not soluble in carbon disulphide, or in any of the solvents which dissolve ordinary phosphorus. Red phosphorus is unaffected by exposure to dry air or oxygen, but in the presence of moisture it is very slowly oxidised. If red phosphorus which has been perfectly freed from ordinary phosphorus, and carefully washed and dried, be exposed to air and moisture, it is found after the lapse of some time to have become acid, owing to slight oxidation into phosphoric acid. When heated in contact with air, red phosphorus does not ignite below a temperature of 240°. Red phosphorus may be obtained in the form of rhombohedral crystals by heating the substance under pressure to a temperature of 580°.

The chief use of phosphorus is in the manufacture of matches. When ordinary phosphorus is employed, the bundles of wooden splints are first tipped with melted paraffin wax, and afterwards dipped into a paste, made of an emulsion of phosphorus, chlorate of potash, and glue. Matches so made ignite when rubbed upon any rough surface; the paraffin (which is sometimes replaced by sulphur) serving to transmit the combustion from the phosphorus to the wood. Since the discovery of red phosphorus, and its non-injurious properties, the old phosphorus match has been largely superseded by the so-called *safety matches*. In these matches the splints are tipped with a mixture of potassium chlorate, potassium dichromate, red lead, and antimony sulphide, and they are ignited by being rubbed upon a prepared surface consisting of a mixture of antimony sulphide and red phosphorus. Although these matches will not ignite by ordinary friction upon any but the specially prepared surface, they may be inflamed by being swiftly drawn along a sheet of ground glass or strip of linoleum.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

Three compounds of phosphorus and hydrogen are known, namely—

PH_3 (gaseous); P_2H_4 (liquid); and $(P_4H_2)_3$ (solid).

GASEOUS HYDROGEN PHOSPHIDE (*Phosphoretted Hydrogen: Phosphine*).

Formula, PH_3. Molecular weight=34.03. Density=17.015.

Modes of Formation.—(1.) This substance is formed when red phosphorus is gently heated in a stream of hydrogen.

(2.) It may be prepared by boiling phosphorus with a solution of potassium or sodium hydroxide—

$$3NaHO + 4P + 3H_2O = 3NaH_2PO_2 + PH_3.$$

In this reaction a small quantity of the liquid hydride (P_2H_4) is simultaneously formed, which imparts to the gas the property of spontaneous inflammability. It also contains a certain quantity of free hydrogen, produced by the action of the caustic alkali upon the sodium hypophosphite, thus—

$$NaH_2PO_2 + 2NaHO = 2H_2 + Na_3PO_4.$$

To obtain the gas by this method, a quantity of a strong solution of caustic soda, and a few fragments of phosphorus, are placed in a flask, fitted as shown in Fig. 122. A stream of coal gas is passed through the apparatus, in order to displace the air, and the solution is gently heated. Hydrogen phosphide is readily disengaged, and as each bubble escapes into the air, it bursts into flame, and forms a vortex ring of white smoke of phosphoric acid.

If alcoholic potash be substituted for the aqueous solution in this reaction, the liquid hydrogen phosphide is dissolved in the alcohol, and the gas which is evolved is therefore not spontaneously inflammable.*

(3.) Hydrogen phosphide is also produced by the action of water upon calcium phosphide—

$$3P_2Ca_2 + 12H_2O = 6Ca(HO)_2 + 4PH_3 + 2P.$$

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* See "Chemical Lecture Experiments," new ed., No. 545.

A secondary reaction, by which liquid hydrogen phosphide is formed, goes on simultaneously—

$$P_2Ca_2 + 4H_2O = 2Ca(HO)_2 + P_2H_4.$$

The gas, therefore, that is evolved is spontaneously inflammable.

(4.) Pure gaseous hydrogen phosphide may be prepared by the action of potassium hydroxide upon phosphonium iodide—

$$PH_4I + KHO = KI + H_2O + PH_3.$$

Properties.—Gaseous hydrogen phosphide, or phosphine, is a colourless gas, having an offensive smell resembling rotten fish. It is not spontaneously inflammable, but its ignition temperature is below 100° C. (see p. 329). The gas burns with a brightly luminous flame, producing water and metaphosphoric acid—

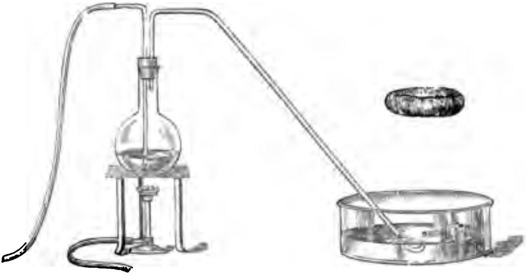


FIG. 122.

$$PH_3 + 2O_2 = HPO_3 + H_2O.$$

When burnt in oxygen the flame is extremely dazzling.

The gas is not acted upon by oxygen at ordinary temperatures and pressures, but if a mixture of these gases be suddenly rarefied, combination at once takes place with explosion. Hydrogen phosphide is decomposed by chlorine or bromine, a jet of the gas spontaneously igniting when introduced into chlorine or the vapour of bromine—

$$PH_3 + 4Cl_2 = 3HCl + PCl_5.$$

The gas is also decomposed by iodine, but in this case the action is less energetic, and a portion of the hydriodic acid which is produced unites with the phosphine and forms phosphonium iodide, thus—

$$(1.)\ PH_3+3I_2=PI_3+3HI.$$
$$(2.)\ PH_3+HI=PH_4I.$$

Phosphine is a highly poisonous gas, and the inhalation of even small quantities of it is attended with injurious effects. It is slightly soluble in water, and imparts its own smell and an unpleasant taste to the liquid. The solution decomposes after a short time, especially in the light, and deposits red phosphorus.

Hydrogen phosphide has no action upon either litmus or turmeric paper, but it resembles its nitrogen analogue, ammonia, in combining with hydrochloric, hydrobromic, and hydriodic acids, forming respectively phosphonium chloride, bromide, and iodide.

Phosphonium Chloride, PH_4Cl.—When a mixture of phosphine and gaseous hydrochloric acid is passed through a tube immersed in a freezing-mixture, the gases unite and form a white crystalline incrustation upon the tube. If the tube be afterwards sealed up, the compound may be sublimed from one part of the tube to another, when it crystallises in large, brilliant, transparent cubes. If the tube be opened, the compound rapidly dissociates into its two generators. This compound may also be obtained by subjecting a mixture of the two gases to pressure. Under a pressure of about eighteen atmospheres at the ordinary temperature, crystals of phosphonium chloride are deposited ; and as the pressure is released the crystals gradually dissociate again.

Phosphonium Bromide, PH_4Br.—Hydrogen phosphide combines with hydrobromic acid at ordinary temperatures and pressures, but as the compound begins to dissociate at the ordinary temperature, the combination is only completely brought about by cooling the gases. Phosphonium bromide may be readily prepared by passing the two gases into a flask immersed in a moderate freezing-mixture. The salt may be obtained in the form of large transparent cubical crystals by sublimation in a sealed vessel.

Phosphonium Iodide, PH_4I.—This compound may be obtained by a method similar to that given for the preparation of the bromide. It is also produced when hydrogen phosphide is passed over iodine, as already mentioned. It is most readily prepared by the action of water upon a mixture of phosphorus and iodine. For this purpose ten parts of phosphorus are dissolved in carbon disulphide in a tubulated retort, to which seventeen parts of iodine are gradually added, the retort being kept cold. The carbon disulphide is then distilled off from a water-bath, a stream of carbon dioxide being passed through the apparatus towards the end of the distillation to assist in expelling the last traces of the disulphide.

Six parts of water are then gradually introduced from a dropping funnel, when a brisk action takes place, and the phosphonium iodide produced is volatilised, and may be condensed in a long wide glass tube connected to the retort. Hydriodic acid is at the same time formed—

$$2I+2P+4H_2O=PH_4I+HI+H_3PO_4.$$

The phosphonium iodide condenses in the form of brilliant quadratic prisms.

Liquid Hydrogen Phosphide, P_2H_4.—This compound is obtained in small quantities when phosphorus is boiled with a solution of caustic soda. It is obtained in large quantities by the decomposition of calcium phosphide with water by the reaction already mentioned. In order to collect the compound a quantity of calcium phosphide is introduced into a flask provided with a dropping funnel and exit tube. After displacing the air from the apparatus by an inert gas water is gradually introduced from the funnel, and the products of the reaction, after passing through a small empty tube where water is arrested, are passed through a U-tube immersed in a freezing-mixture, where the liquid hydrogen phosphide condenses.

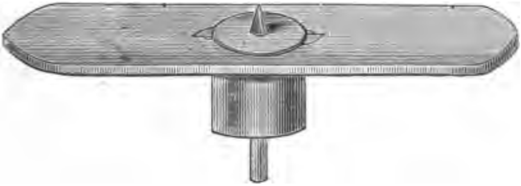


FIG. 123.

Properties.—Liquid hydrogen phosphide is a colourless, highly refracting, and spontaneously inflammable liquid. On exposure to light it is quickly decomposed into the gaseous and the solid hydrides of phosphorus—

$$5P_2H_4=P_4H_2+6PH_3.$$

The formation of a spontaneously inflammable gas by the action of water upon calcium phosphide has found a practical application in the marine appliance known as "Holmes' signal." This consists of a tin canister filled with lumps of calcium phosphide. A metal tube, closed at the bottom with a piece of block tin, enters the canister from below, and a short cone of the same soft metal is soldered upon the top. When the signal is to be used it is securely fixed into a wooden float (Fig. 123). The cone is cut off and a hole punctured through the bottom of the tube below, and the apparatus thrown into the sea. The hydrogen phosphide spontaneously ignites and burns with a large brilliant flame from the top of the tin, illuminating a considerable area.

Solid Hydrogen Phosphide, $(P_4H_2)_3$ or $P_{12}H_6$, is a yellow powder, obtained, as already mentioned, by the spontaneous decomposition of the liquid compound. Recent determinations* of its molecular weight prove that its molecular composition is expressed by the formula $P_{12}H_6$.

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorus combines with all the halogen elements, forming the following compounds—

PF_3 PCl_3 PBr_3 PI_3.
PF_5 PCl_5 PBr_5 P_2I_4.

Phosphorus Trifluoride, PF_3, is obtained by the action of arsenic trifluoride upon phosphorus trichloride—

$$AsF_3 + PCl_3 = PF_3 + AsCl_3.$$

It is more conveniently prepared by gently heating a mixture of zinc fluoride and phosphorus tribromide—

$$3ZnF_2 + 2PBr_3 = 2PF_3 + 3ZnBr_2.$$

Properties.—Phosphorus trifluoride is a colourless, pungent-smelling gas. It has no action upon glass in the cold, but when heated it forms silicon fluoride and phosphorus. It is moderately soluble in water. Phosphorus trifluoride unites directly with bromine, forming the compound PF_3Br_2.

Phosphorus Pentafluoride, PF_5.—This compound is formed when phosphorus burns in fluorine. It is best prepared by the action of arsenic trifluoride upon phosphorus pentachloride—

$$5AsF_3 + 3PCl_5 = 3PF_5 + 5AsCl_3.$$

---

* Schenck and Buck, *Berichte*, 1904.

Properties.—Phosphorus pentafluoride is a heavy, colourless gas, which fumes strongly in moist air, being decomposed by water into hydrofluoric and phosphoric acids—

$$PF_5+4H_2O=5HF+H_3PO_4.$$

Owing to this decomposition it has a pungent and irritating effect upon the mucous membrane.

It is not acted upon by oxygen, but unites directly with dry gaseous ammonia, forming a white solid compound having the composition $2PF_5,5NH_3$.

Phosphorus pentafluoride is an extremely stable compound, being capable of withstanding a very high temperature without dissociation. On this account it is of special interest, as affording an example of a compound in which phosphorus is united to five monovalent atoms to form a stable substance. The corresponding chlorine and bromine compounds readily dissociate, when heated, into compounds containing trivalent phosphorus and the free halogen.

Phosphorus Trichloride, PCl_3.—This compound is prepared by passing dry chlorine over red phosphorus, gently heated in a tubulated retort. The two elements readily combine, and the volatile trichloride, mixed with more or less of the pentachloride, distils off, and is collected in a well-cooled receiver. The product is freed from the higher chloride by redistillation over ordinary phosphorus.

Properties.—Phosphorus trichloride is a colourless, mobile liquid, which boils at 75.95°. It has a pungent smell, and fumes strongly in moist air. Water at once decomposes it into hydrochloric and phosphorous acids—

$$PCl_3+3H_2O=H_3PO_3+3HCl.$$

Phosphorus Pentachloride, PCl_5.—This compound is formed when phosphorus burns in excess of chlorine. It is prepared by the action of chlorine upon the trichloride. Dry chlorine is passed on to the surface of a quantity of the trichloride, contained in a flask which is kept cool. The absorption of the chlorine is attended with considerable rise of temperature, and the contents of the flask rapidly become converted into a dry, pale-yellow solid.

Phosphorus pentachloride is conveniently obtained by passing chlorine through a solution of phosphorus in carbon disulphide, the solution being kept cold.

Properties.—Phosphorus pentachloride is a yellowish-white, crystalline solid, having a pungent and irritating odour. It fumes strongly in contact with moist air, being decomposed by moisture into hydrochloric acid and phosphorus oxychloride—

$$PCl_5 + H_2O = 2HCl + POCl_3.$$

With excess of water, both phosphorus oxychloride and phosphorus pentachloride dissolve with evolution of heat, forming hydrochloric and phosphoric acids—

$$\begin{aligned} POCl_3 &+ 3H_2O = H_3PO_4 + 3HCl. \\ PCl_5 &+ 4H_2O = H_3PO_4 + 5HCl. \end{aligned}$$

Phosphorus pentachloride readily sublimes, without melting, at a temperature below that of boiling water. It can only be melted by being heated under pressure to a temperature of 148°.

As the vapour of phosphorus pentachloride is heated, the compound dissociates into phosphorus trichloride and free chlorine. At 300° this dissociation is complete, and the vapour consists of equal molecules of the trichloride and chlorine. The gradual breaking down of the molecules of pentachloride is seen from the following table, which gives the densities of the gas at different temperatures—

Temperatures	182°	200°	250°	300°
Density . .	72.5	69.2	57.0	52.06

At 300° it consists of molecules of PCl_3 (molecular weight = 137.35) and molecules of chlorine (molecular weight = 70.90) in equal numbers, which theoretically gives the molecular weight—

$$\frac{137.35 + 70.90}{4} = 52.06.$$

Phosphorus pentachloride is an important chemical reagent, inasmuch as by its action upon oxyacids, both inorganic and organic, the (HO) group in the acid can be replaced by chlorine. Thus with sulphuric acid, chlorosulphuric acid is formed—

$$\left.\begin{matrix} HO \\ HO \end{matrix}\right\} SO_2 + PCl_5 = \left.\begin{matrix} Cl \\ HO \end{matrix}\right\} SO_2 + POCl_3 + HCl.$$

With acetic acid it yields acetyl chloride—

$$\left.\begin{matrix}\mathrm{HO}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CO}+\mathrm{PCl_5}=\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CO}+\mathrm{POCl_3}+\mathrm{HCl}.$$

It also effects the replacement of (HO) by chlorine, in alcohols. Thus, with ethyl alcohol (spirits of wine) it forms ethyl chloride—

$$\left.\begin{matrix}\mathrm{HO}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CH_2}+\mathrm{PCl_5}=\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{CH_3}\end{matrix}\right\}\mathrm{CH_2}+\mathrm{POCl_3}+\mathrm{HCl}.$$

Phosphorus Tribromide, PBr_3, is best prepared by dropping bromine upon an excess of red phosphorus. It forms a colourless pungent-smelling liquid, which boils at 172.9°.

Phosphorus Pentabromide, PBr_5, is prepared by adding bromine to the tribromide. It is a yellow solid, which melts to a reddish liquid. It is very unstable, being dissociated below 100° into its generators, the tribromide and bromine.

Diphosphorus Tetriodide (*phosphorus di-iodide*), P_2I_4.—This substance is prepared by the gradual addition of 8.2 parts of iodine to 1 part of phosphorus dissolved in carbon disulphide. On gently distilling off the carbon disulphide, the iodide is left as a yellow crystalline solid. The compound melts at 110°.

Phosphorus Tri-iodide, PI_3, is obtained by employing a larger proportion of iodine in the above reaction. It is a solid substance, crystallising in red six-sided prisms, which are decomposed by water into hydriodic and phosphorus acids.

OXY AND THIO COMPOUNDS OF PHOSPHORUS AND THE HALOGENS.

The following compounds are known, containing phosphorus combined with the halogens, and either oxygen or sulphur—

$$\begin{array}{lllll}\mathrm{POF_3}; & \mathrm{POCl_3}; & \mathrm{P_2O_3Cl_4}; & \mathrm{POBrCl_2}; & \mathrm{POBr_3}.\\ \mathrm{PSF_3}; & \mathrm{PSCl_3}; & — & — & \mathrm{PSBr_3}.\end{array}$$

These compounds may be regarded as derived from the haloid compounds, by the replacement of two atoms of the halogen by an equivalent of oxygen or of divalent sulphur; or they may be viewed as derivatives of phosphoric acid, by the substitution of halogen elements in the place of (HO) groups. The tribasic phosphoric acid, $PO(HO)_3$, may be regarded as giving rise to the compounds POF_3, $POCl_3$, &c.; while the compound $P_2O_3Cl_4$ may be viewed as a derivative of pyrophosphoric acid, $P_2O_3(HO)_4$.

Phosphoryl Fluoride (*phosphorus oxyfluoride*), POF_3, may be obtained by the action of phosphoryl chloride ($POCl_3$) upon zinc fluoride—

$$3ZnF_2+2POCl_3=2POF_3+3ZnCl_2.$$

It may also be prepared by gently heating a mixture of finely powdered cryolite and phosphorus pentoxide—

$$2(AlF_3,3NaF)+2P_2O_5=4POF_3+Al_2O_3+3Na_2O.$$

Phosphoryl fluoride is a colourless gas, which fumes in the air, and is decomposed by water. The gas in a dry condition does not attack glass.

Thiophosphoryl Fluoride, PSF_3, is most readily prepared by gently heating in a leaden tube a mixture of dry lead fluoride and phosphorus pentasulphide—

$$3PbF_2+P_2S_5=3PbS+2PSF_3.$$

The gas may be collected over mercury.

Thiophosphoryl fluoride is a colourless gas, which spontaneously inflames when a jet of it is allowed to escape into the air. It burns with a pale greenish non-luminous flame. In pure oxygen the gas burns with a yellow and more luminous flame. The gas is decomposed by heat into phosphorus fluoride, phosphorus, and sulphur. When heated in a glass vessel, sulphur and phosphorus are deposited, and silicon tetrafluoride is formed—

$$4PSF_3+3Si=3SiF_4+4P+4S.$$

Phosphoryl Chloride (*phosphorus oxychloride*), $POCl_3$.—This compound is formed by the first action of water upon phosphorus pentachloride (*q.v.*). It is also obtained when phosphorus pentachloride and pentoxide are heated together in a sealed tube—

$$3PCl_5+P_2O_5=5POCl_3.$$

It is most readily prepared by heating phosphorus pentachloride with either oxalic acid or boric acid, thus—

$$PCl_5+H_2C_2O_4=POCl_3+2HCl+CO_2+CO.$$
$$3PCl_5+2H_3BO_3=3POCl_3+6HCl+B_2O_3.$$

Properties.—Phosphoryl chloride is a colourless fuming liquid, which boils at 107.23.° When cooled to about − 10° it solidifies to a white crystalline mass, which melts at 0.8°. It is decomposed by water with formation of tribasic phosphoric acid and hydrochloric acid—

$$POCl_3+3H_2O=PO(HO)_3+3HCl.$$

Pyrophosphoryl Chloride, $P_2O_3Cl_4$, is obtained by passing nitrogen peroxide through phosphorus trichloride, and subsequently distilling the liquid. The reaction is complicated, and cannot be expressed by a single equation ; nitrogen is evolved, and phosphorus pentoxide, nitrosyl chloride, and phosphoryl chloride are simultaneously formed. Pyrophosphoryl chloride is a colourless fuming liquid, boiling between 210° and 215°. It is decomposed by water, and forms hydrochloric acid and orthophosphoric acid (*not pyrophosphoric acid*)—

$$P_2O_3Cl_4+5H_4O=2H_3PO_4+4HCl.$$

It is converted by phosphorus pentachloride into phosphoryl chloride—

$$P_2O_3Cl_4+PCl_5=3POCl_3.$$

Thiophosphoryl Chloride, $PSCl_3$, is prepared by heating a mixture of phosphorus pentasulphide and pentachloride—

$$3PCl_5+P_2S_5=5PSCl_3.$$

It is a colourless liquid, boiling at 125°. It fumes in moist air, being decomposed by water into sulphuretted hydrogen, phosphoric and hydrochloric acids—

$$PSCl_3+4H_2O=H_2S+H_3PO_4+3HCl.$$

OXIDES AND OXYACIDS OF PHOSPHORUS.

Four compounds of phosphorus and oxygen are known, all of which are formed when phosphorus is burned in a limited supply of air—

Phosphorus monoxide	*P_4O?*
Phosphorous oxide (phosphorus trioxide) .	P_4O_6.
Phosphorus tetroxide	P_2O_4.
Phosphoric oxide (phosphorus pentoxide) .	P_2O_5.

The two compounds, phosphorus trioxide and pentoxide, are the best known of these oxides, and they give rise respectively to phosphorous and phosphoric acids. The following oxyacids of phosphorus are known—

		Corresponding Oxide.
Hypophosphorous acid	H_3PO_2 —	—
Phosphorous acid . .	H_3PO_3 or $P(HO)_3$.	P_4O_6
Orthophosphoric acid .	H_3PO_4 „ $PO(HO)_3$	P_2O_5
Pyrophosphoric acid .	$H_4P_2O_7$ „ $P_2O_3(HO)_4$	
Metaphosphoric acid .	HPO_3 „ $PO_2(HO)$	

When phosphorus is dissolved in a solution of aqueous alcoholic potash, and dilute hydrochloric acid is added, a yellow or reddish precipitate is obtained which was believed to have the composition P_4O. Recent investigations, however, seem to prove that the substance so obtained is identical with red phosphorus. (*Chem. Soc. Journal*, Nov. 1899, and Nov. 1901.)

Phosphorous Oxide (*phosphorous anhydride*), P_4O_6; molecular weight = 220.—This oxide is obtained, mixed with a large excess of the pentoxide, when phosphorus is burned in a tube through which a regulated stream of air is passed. In order to obtain the compound in a state of purity, the following method is employed. A quantity of phosphorus is introduced into a glass tube bent in the manner indicated in Fig. 124, and fitted into one end of a long, wide, Liebig's condenser. Into the end of the condenser nearest to the U-tube there is introduced a loose plug of glass wool, which serves to arrest the pentoxide. The phosphorus is ignited at the open end of the glass tube, and a stream of air drawn through the apparatus by means of an aspirator. A stream of water, at 60°, is circulated through the condenser, when the easily fusible phosphorous oxide is carried over, and condenses in the U-tube, which is immersed in a freezing-mixture.

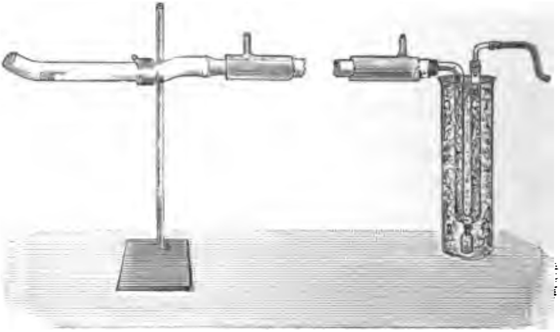


FIG. 124.

Properties.—Phosphorous oxide, as it collects in the cooled tube, is a snow-white crystalline solid, which melts at 22.5° to a colourless liquid. The liquid solidifies at 21° to a white, waxy-looking mass, consisting of monoclinic prismatic crystals. The liquid boils at 173.1. It possesses an unpleasant garlic smell, and is highly poisonous. Phosphorous oxide is only very slowly acted upon by cold water, which gradually dissolves it, forming phosphorous acid—

$$P_4O_6+6H_2O=4H_3PO_3.$$

In contact with hot water a violent action takes place, in which spontaneously inflammable phosphoretted hydrogen is evolved, and a red deposit, consisting of red phosphorus, is formed.

When heated in a sealed tube to a temperature of 440°, phosphorous oxide is decomposed into phosphorus tetroxide, and red phosphorus—

$$2P_4O_6=3P_2O_4+2P.$$

When exposed to air or oxygen, phosphorous oxide is gradually oxidised into phosphorus pentoxide, but when placed in warm oxygen it bursts into flame. When brought into chlorine it also spontaneously inflames.

Phosphorus Tetroxide, P_2O_4.—This substance is obtained when phosphorous oxide is heated in a sealed tube to a temperature of 440°. It forms brilliant transparent crystals, which appear as a sublimate in the tube. This oxide is highly deliquescent, and dissolves in water with evolution of heat.

FIG. 125.

Phosphoric Oxide, P_2O_5 (or P_4O_{10}).—This oxide is the main product of the combustion of phosphorus in air or oxygen. It may readily be obtained by burning a quantity of phosphorus in a small capsule, and covering the whole with a large bell-jar (Fig. 125). The white clouds of phosphoric oxide (or phosphorus pentoxide) collect as a soft snow-like substance.

Properties.—Phosphorus pentoxide is a white, amorphous, and very voluminous powder. It is without smell, although as usually prepared it frequently possesses a slight garlic odour, owing to the presence of phosphorous oxide. At a temperature short of a red heat this oxide vaporises, and recent determinations of its vapour-density point to the conclusion that the compound under these conditions has a composition expressed by the formula P_4O_{10}.

Phosphoric oxide is extremely hygroscopic, absorbing moisture from the air with great rapidity. It must therefore be preserved either in well-fitting stopper bottles or in hermetically sealed vessels. Its affinity for water constitutes it the most useful desiccating agent known to chemists : prolonged exposure to phosphoric oxide removes the last traces of aqueous vapour from gases.

When thrown into water, phosphoric oxide is dissolved with a hissing sound resembling the quenching of hot iron, and forms metaphosphoric acid—

$$P_2O_5+H_2O=2HPO_3,$$

which gradually passes into orthophosphoric acid—

$$HPO_3+H_2O=H_3PO_4.$$

Phosphoric oxide reacts with a number of substances, both inorganic and organic, removing oxygen and hydrogen from them in the proportion in which these elements form water; thus, it converts nitric acid into nitrogen pentoxide—

$$2HNO_3-H_2O=N_2O_5.$$

In the same way it withdraws the elements of water from alcohol, with the evolution of ethylene—

$$C_2H_6O-H_2O=C_2H_4.$$

Hypophosphorous Acid, H_3PO_2.—This acid is prepared by the action of sulphuric acid upon the barium salt—

$$Ba(H_2PO_2)_2+H_2SO_4=BaSO_4+2H_3PO_2.$$

The solution, after the removal of the barium sulphate by filtration, is gently heated until its temperature rises to 130°, when it will be sufficiently concentrated to deposit crystals when cooled to 0°.

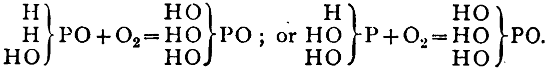
The barium hypophosphite is obtained by boiling phosphorus with a solution of barium hydroxide—

$$3Ba(HO)_2+8P+6H_2O=2PH_3+3Ba(H_2PO_2)_2.$$

Properties.—Hypophosphorous acid is a white crystalline compound which melts at 17.4°. When strongly heated it is converted into orthophosphoric acid, with the evolution of gaseous hydrogen phosphide—

$$2H_3PO_2=H_3PO_4+PH_3.$$

Hypophosphorous acid acts as a powerful reducing agent, on account of the readiness with which it absorbs oxygen and is converted into orthophosphoric acid—



$$\left.\begin{matrix}H\\H\\HO\end{matrix}\right\}PO+O_2=\left.\begin{matrix}HO\\HO\\HO\end{matrix}\right\}PO\text{ ; or }\left.\begin{matrix}H\\HO\\HO\end{matrix}\right\}P+O_2=\left.\begin{matrix}HO\\HO\\HO\end{matrix}\right\}PO.$$

Thus if hypophosphorous acid or the sodium salt in solution be added to a solution of copper sulphate, and the mixture gently warmed, the copper is reduced even a stage further than to the metallic state, and a dark red-brown precipitate of *copper hydride*, Cu_2H_2, is obtained, thus—

$$3NaH_2PO_2+4CuSO_4+6H_2O=3H_3PO_4+H_2SO_4 \\ +3HNaSO_4+2Cu_2H_2.$$

This constitutes a characteristic reaction for hypophosphites.

Hypophosphorous acid is a feeble monobasic acid ; its salts with monovalent metals being represented by the formula MH_2PO_2.

It is customary to express the basicity of oxyacids by the number of (HO) groups that are contained in the molecule, and as this acid is monobasic its constitution would be expressed by the formula $POH_2(HO)$. Many of the oxyacids of phosphorus, however, show a tendency to exhibit a lower degree of basicity than is represented by the number of (HO) groups they contain; thus, orthophosphoric acid, $PO(HO)_3$, which is tribasic, and forms the salt trisodium phosphate, $PO(NaO)_3$, holds the third atom of the metal so loosely that even such a feeble acid as carbonic acid is capable of expelling it—

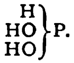
$$PO(NaO)_3+CO_2+H_2O=PO(HO)(NaO)_2+HNaCO_3.$$

or—

$$Na_3PO_4+CO_2+H_2O=HNa_2PO_4+HNaCO_3.$$

The weaker acid, phosphorous acid, is also tribasic, $P(HO)_3$, and forms trisodium phosphite, $P(NaO)_3$, or Na_3PO_3. But this salt is even decomposed by water, into the disodium phosphite, $P(HO)(NaO)_2$, or HNa_2PO_3.

Hypophosphorous acid being a still weaker acid, its acidic power is destroyed as soon as one atom of hydrogen is replaced by a base, and its constitution may, in harmony with these facts, be expressed by the formula $PH(HO)_2$, or



$$\left.\begin{matrix}H\\HO\\HO\end{matrix}\right\}P.$$

Phosphorous Acid, H_3PO_3, or $P(HO)_3$.—As already mentioned, this acid is formed when phosphorous oxide is dissolved in cold water.

It is most readily prepared by the action of water upon phosphorus trichloride—

$$PCl_3+3H_2O=3HCl+P(HO)_3.$$

The production and decomposition of the phosphorus trichloride may be carried on simultaneously, by passing a stream of chlorine through phosphorus which is melted beneath water. The solution is evaporated until its temperature rises to 180°, when the liquid will have become so concentrated that on cooling it solidifies to a crystalline mass.

Properties.—Phosphorous acid is a white crystalline substance which melts at 70.1°. When heated, it decomposes into orthophosphoric acid, with evolution of hydrogen phosphide—

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

Like hypophosphorous acid, this compound absorbs oxygen, and therefore is a powerful reducing agent; silver salts are reduced to metallic silver, and mercuric salts are reduced to mercurous salts. By the absorption of oxygen it is converted into orthophosphoric acid—

$$H_3PO_3 + O = H_3PO_4.$$

Although a tribasic acid, its tribasic salts are unstable; the sodium compound, Na_3PO_3, which is the most stable inorganic salt, is decomposed by water into the dibasic salt—

$$Na_3PO_3 + H_2O = HNa_2PO_3 + NaHO.$$

or $$\left.\begin{matrix}NaO\\NaO\\NaO\end{matrix}\right\}P + H_2O = \left.\begin{matrix}HO\\NaO\\NaO\end{matrix}\right\}P + NaHO.$$

Orthophosphoric Acid, H_3PO_4, or $PO(HO)_3$.—This acid is formed when phosphorus pentoxide is dissolved in boiling water, or when the solution of the oxide in cold water is boiled—

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

Orthophosphoric acid is readily obtained by the oxidation of red phosphorus with nitric acid. Copious red fumes are evolved, and phosphoric acid remains in solution.

Phosphoric acid is prepared on a large scale by the action of sulphuric acid upon bone ash, as in the process for the manufacture of phosphorus—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The calcium sulphate is removed by filtration, and the solution evaporated to a syrup. Prepared in this way the acid usually contains arsenic. This is removed by first reducing it to arsenious oxide by means of sulphur dioxide, and after boiling off the excess of sulphur dioxide, precipitating the arsenic as sulphide by means of sulphuretted hydrogen.

Properties.—The solution obtained by these methods is either concentrated in vacuo or heated to a temperature of 140°, and allowed to cool, when the acid is obtained in the form of transparent six-sided prismatic crystals belonging to the rhombic system. The substance is deliquescent, and melts at 38.6°.

Phosphoric acid is tribasic, and forms three series of salts, according as one, two, or three of its hydrogen atoms are replaced by an equivalent of metal. Thus, with the metal sodium the three salts are known—

Dihydrogen sodium phosphate	H_2NaPO_4.
Hydrogen disodium phosphate	HNa_2PO_4.
Trisodium phosphate (normal sodium phosphate)	Na_3PO_4.

The hydrogen may be replaced by its equivalent of more than one base. Thus, the well-known compound, *microcosmic salt*, is hydrogen sodium ammonium phosphate, $HNa(NH_4)PO_4,4H_2O$. The salt, which is precipitated when magnesium sulphate (in the presence of ammonium chloride and ammonia) is added to a solution of a phosphate, consists of the compound ammonium magnesium phosphate $(NH_4)MgPO_4,6H_2O$.

The heavy metals usually only form normal phosphates. Thus, on the addition of silver nitrate to a solution of either of the three sodium salts, the same silver salt is precipitated, namely, triargentic phosphate.

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$
*$$HNa_2PO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$
$$H_2NaPO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3.$$

Pyrophosphoric Acid, $H_4P_2O_7$, or $P_2O_3(HO)_4$.—This acid is derived from orthophosphoric acid by the withdrawal of one molecule of water from two molecules of the acid. This change is effected by heating the *ortho* acid to 213°—

$$2H_3PO_4 - H_2O = H_4P_2O_7.$$

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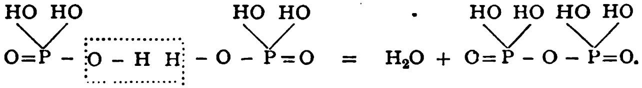
[*] Hydrogen disodium phosphate, although belonging to that class of compounds commonly called *acid salts*, on account of the fact that it still retains a portion of the replaceable hydrogen of the acid, is strongly *alkaline* in its action upon litmus; silver nitrate is a neutral compound, hence in this reaction, by mixing an alkaline and a neutral liquid, an *acid* liquid is obtained, on account of the molecule of nitric acid that is set free.

The formation of this acid from two molecules of orthophosphoric acid will be made clear by the following formulæ—



$$O{=}\overset{HO\quad HO}{P}-\boxed{O-H\quad H}-O-\overset{HO\quad HO}{P}{=}O \;=\; H_2O + O{=}\overset{HO\quad HO}{P}-O-\overset{HO\quad HO}{P}{=}O.$$

Pyrophosphates are formed when monohydrogen orthophosphates are heated. Thus, by heating hydrogen disodium orthophosphate, sodium pyrophosphate is formed—

$$2HNa_2PO_4 - H_2O = Na_4P_2O_7.$$

When ammonium magnesium phosphate (see above) is heated in the same way it loses water and ammonia, and is transformed into magnesium pyrophosphate, thus—

$$2(NH_4)MgPO_4 = Mg_2P_2O_7 + H_2O + 2NH_3.$$

Properties.—Pyrophosphoric acid is an opaque white crystalline solid, readily soluble in water. Its aqueous solution passes slowly into orthophosphoric acid, the change taking place rapidly on boiling; a solution of this acid, therefore, cannot be concentrated by boiling.

The pyrophosphates are stable salts, and their solutions may be boiled without change; by boiling with acids, however, they are converted into orthophosphates.

Metaphosphoric Acid, HPO_3 or $PO_2(HO)$.—This acid is formed when phosphorus pentoxide is allowed to deliquesce. It may be obtained by the abstraction of one molecule of water from one molecule of orthophosphoric acid, which is brought about by heating the tribasic acid to redness—

$$H_3PO_4 - H_2O = HPO_3.$$

It is also obtained by strongly heating pyrophosphoric acid—

$$H_4P_2O_7 - H_2O = 2HPO_3.$$

The sodium salt is obtained by strongly igniting either dihydrogen sodium phosphate, H_2NaPO_4, or hydrogen sodium ammonium phosphate (*microcosmic salt*), $HNa(NH_4)PO_4$; or dihydrogen sodium pyrophosphate, $H_2Na_2P_2O_7$.

Properties.—Metaphosphoric acid is a transparent vitreous solid (frequently termed *glacial phosphoric acid*). It is readily fusible, and is usually cast into sticks. At a high temperature it may be volatilised. Metaphosphoric acid is easily soluble in water, and its solution is slowly transformed into orthophosphoric acid ; this change takes place rapidly on boiling, and the acid passes directly into the tribasic acid without the intermediate formation of pyrophosphoric acid—

$$HPO_3 + H_2O = H_3PO_4.$$

Metaphosphoric acid is monobasic, but it possesses the remarkable property of forming a number of salts which may be regarded as derived from several hypothetical polymeric varieties of the acid.

Monometaphosphoric acid, HPO_3,	forms	monometaphosphates, $NaPO_3$.
Dimetaphosphoric acid, $(HPO_3)_2$	,,	dimetaphosphates, $K_2P_2O_6$.
Trimetaphosphoric acid, $(HPO_3)_3$	,,	trimetaphosphates, $Na_3P_3O_9$.
Tetrametaphosphoric acid, $(HPO_3)_4$,	,,	tetrametaphosphates, $Pb_2P_4O_{12}$.
Hexametaphosphoric acid, $(HPO_3)_6$,	,,	hexametaphosphates, $Na_6P_6O_{18}$.

The three compounds, ortho-, pyro-, and metaphosphoric acids, are readily distinguished from each other by means of silver nitrate and their action upon albumen :—

Reagent.	Orthophosphoric Acid.	Pyrophosphoric Acid.	Metaphosphoric Acid.
Silver nitrate .	Canary yellow precipitate of Ag_3PO_4	White crystalline precipitate of $Ag_4P_2O_7$	White gelatinous precipitate of $AgPO_3$
Albumen . .	No action	No action	Coagulates

Orthophosphoric acid is also distinguished by giving a yellow precipitate of ammonium phospho-molybdate upon the addition of excess of a solution of ammonium molybdate in nitric acid (see Molybdenum).

Compounds of Phosphorus containing Nitrogen.—By the action of ammonia upon phosphorus pentachloride, and upon phosphoryl chloride ($POCl_3$), a number of nitrogen derivatives are obtained. Thus, when gaseous ammonia is passed over phosphorus pentachloride, and the solid mass so obtained is heated in a stream of an inert gas until the ammonium chloride is driven off, a white insoluble powder remains having the composition represented by the formula PN(NH), to which the name *phospham* has been given—

$$PCl_5 + 7NH_3 = 5NH_4Cl + PN(NH).$$

Phosphoryl Triamide, $PO(NH_2)_3$, is obtained by the action of gaseous ammonia upon phosphoryl chloride—

$$POCl_3+6NH_3=PO(NH_2)_3+3NH_4Cl.$$

When heated out of contact with air, phosphoryl triamide yields ammonia and *phosphoryl nitride*, thus—

$$PO(NH_2)_3=2NH_3+PON.$$

Pyrophosphamic Acids.—Three of these compounds are known, which may be regarded as pyrophosphoric acid, in which 1, 2, and 3 of the (HO) groups have been replaced respectively by the group (NH_2), thus—

Pyrophosphoric acid	$P_2O_3(HO)_4$.
Pyrophosphamic acid	$P_2O_3(HO)_3(NH_2)$.
Pyrophosphodiamic acid . . .	$P_2O_3(HO)_2(NH_2)_2$.
Pyrophosphotriamic acid . . .	$P_2O_3(HO)(NH_2)_3$.

Compounds of Phosphorus with Sulphur.—A number of compounds of phosphorus and sulphur have been obtained by heating together varying proportions of sulphur and red phosphorus. The following compounds are known:—

		Analogous Oxides.
Phosphorus monosulphide. . .	P_4S . .	—
Phosphorus sesquisulphide . .	P_4S_3 . .	—
Phosphorus trisulphide . . .	P_2S_3 . .	P_4O_6
Phosphorus tetrasulphide (?) . .	P_2S_4 . .	P_2O_4
Phosphorus pentasulphide . .	P_2S_5 . .	P_2O_5

Phosphorus Pentasulphide, P_2S_5.—This compound is the best-known member of the series. It is prepared by gently heating red phosphorus and fragments of sulphur, in the proportion required by the formula, in a flask. The elements combine with energy, and on cooling a solid mass is obtained. This solid material is then distilled in a current of carbon dioxide, when the pentasulphide is obtained in the form of yellow crystals. The compound may also be obtained by dissolving ordinary phosphorus and sulphur in the proper proportions in carbon disulphide and heating the solution in sealed tubes to 210°. On allowing the solution to cool, yellow crystals of the pentasulphide are deposited. Phosphorus pentasulphide is decomposed by water with the formation of orthophosphoric acid and the evolution of sulphuretted hydrogen—

$$P_2S_5+8H_2O=2H_3PO_4+5H_2S.$$

ARSENIC.

Symbol, As. Atomic weight = 75. Molecular weight = 300.
Vapour density = 150.

Occurrence.—Arsenic is found in the free state in nature, usually in the form of small nodules, more rarely as distinct crystals. In combination with sulphur it constitutes the minerals *realgar*, or *ruby sulphur*, As_2S_2, and *orpiment*, As_2S_3. In combination with metals, as arsenides, it occurs widely distributed, the commonest ores being *arsenical iron*, $FeAs_2$ and Fe_4As_3; *kupfernickel*, NiAs and $NiAs_2$; and *tin white cobalt*, $CoAs_2$. With metals and sulphur it is met with in such minerals as *arsenical pyrites*, *mispickel*, or *white mundic*, FeS_2, $FeAs_2$; *cobalt glance*, CoS_2,$CoAs_2$; *nickel glance*, NiS_2,$NiAs_2$. Arsenic is present in small quantities in most samples of iron pyrites, hence it finds its way into sulphuric acid manufactured from pyrites. It also occurs in coal smoke, being derived from the pyrites contained in coal, and hence is present in the atmosphere: during the prevalence of yellow fogs the amount of arsenic present is very appreciable.

Modes of Formation.—On the small scale, arsenic is obtained by heating a mixture of arsenious oxide, As_4O_6, with powdered charcoal—

$$As_4O_6 + 6C = 6CO + 4As.$$

On a larger scale it is usually obtained either from native arsenic or from arsenical pyrites; the latter substance, when heated, gives up arsenic, and ferrous sulphide is left behind—

$$FeS_2,FeAs_2 = 2As + 2FeS.$$

The mineral is heated in long narrow horizontal earthenware retorts, into whose mouths are fitted earthenware receivers. The arsenic volatilises and condenses in these receivers as a compact crystalline solid. It is purified by redistillation.

Properties.—Arsenic which has been resublimed is a brilliant steel-grey metallic-looking substance, forming hexagonal rhombohedral crystals, having a specific gravity of 5.62 to 5.96. It is very brittle, and is a good conductor of heat and electricity. Arsenic begins to volatilise at 100°, and rapidly vaporises at a dark-red heat, passing from the solid to the vaporous states without liquefying. The vapour has a yellow colour and an unpleasant garlic smell. When heated under pressure arsenic melts at 500°, and on cooling solidifies to a compact crystalline mass. When arsenic is vaporised in a glass tube, in a current of hydrogen, it condenses along the tube in three distinct conditions: that which is deposited nearest to the heated portion of the tube is in the form of rhombohedral crystals; that which sublimes a little farther along, and condenses at a point where the temperature is about 210°-220°, consists of a black shining amorphous deposit; while at a still more distant and cooler portion of the tube a grey crystalline sublimate is formed. These are regarded as allotropic modifications of arsenic. The amorphous variety is also formed, when arsenic hydride is decomposed by being passed through a heated tube (*q.v.*). Amorphous arsenic is unacted upon by air at ordinary temperatures, and only slightly oxidised at 80°. The grey crystalline variety is readily oxidised on exposure to air at ordinary temperatures.

Amorphous arsenic, when heated out of contact with air to 360°, is converted into the rhombohedral variety.

Arsenic, like phosphorus, forms tetratomic molecules, its molecular weight as deduced from its vapour-density being $75 \times 4 = 300$.

When heated in oxygen arsenic burns with a bright bluish-white flame, forming arsenious oxide, As_4O_6. It is oxidised by sulphuric acid, nitric acid, and other oxidising agents. It combines readily with chlorine, and when thrown into this gas in the condition of powder it spontaneously inflames, forming arsenic trichloride. Thrown into bromine a fragment of arsenic spontaneously inflames, and burns as it floats about upon the surface of the liquid.

Arsenic, in many of its characteristics, resembles the true metals; it is one of those elements lying on the borderland between true metals and non-metals, to which the name *metalloid* is applied. It is capable of forming alloys with metals, and an alloy of this element with lead is employed for the manufacture of shot. It is found that by the addition of a small proportion of arsenic to lead the melted metal is more fluid, and therefore more readily assumes the spheroidal form when projected from the *shot tower*, and on solidification the alloy is considerably harder than pure lead.

ARSENIC HYDRIDE (*Arsenuretted Hydrogen. Arsine*).

Formula, AsH_3. Molecular weight = 78.03. Density = 39.015.

Modes of Formation.—(1.) Arsenic hydride is formed when soluble arsenic compounds are exposed to the action of nascent hydrogen: thus, when a solution of arsenious oxide is introduced into a mixture from which hydrogen is being generated, such as zinc or iron and dilute hydrochloric or sulphuric acid, arsenic hydride is obtained, mixed with free hydrogen—

$$As_4O_6 + 24H = 4AsH_3 + 6H_2O.$$

(2.) By the same action of nascent hydrogen, arsenic hydride is formed when a solution of either arsenious oxide, As_4O_6, or arsenic oxide, As_2O_5, is subjected to electrolysis.

(3.) Arsenic hydride is also formed when arsenical compounds are in contact with organic matter which is undergoing decomposition. During the growth of certain moulds and fungi a small quantity of hydrogen is evolved, which by its action upon the arsenic compound, gives rise to the formation of arsenic hydride. By this action arsenic hydride is sometimes formed in dwelling-houses where arsenical wall-papers are employed, and where, from dampness or other causes, mould develops.*

(4.) Pure arsenic hydride is prepared by the action of dilute hydrochloric or sulphuric acid upon an alloy of arsenic and zinc—

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4,$$

or by the action of either water or dilute acid upon an alloy of arsenic and sodium, prepared by heating sodium in the impure arsenic hydride obtained by method No. 1.

Properties.—Arsenic hydride is a colourless, offensive-smelling, and highly poisonous gas. Under pressure it condenses to a colourless liquid, which boils at $-54.8°$ and solidifies at $-113.5°$. The gas burns with a lilac-coloured flame, forming water and white fumes of arsenious oxide—

$$4AsH_3 + 6O_2 = As_4O_6 + 6H_2O.$$

When the supply of air to the flame is limited, as when a cold surface is depressed upon it, water is formed and arsenic is deposited as a shining black amorphous film—

$$4AsH_3 + 3O_2 = As_4 + 6H_2O.$$

Arsenic hydride is readily decomposed by heat into its elements: hus, when the gas is passed through a glass tube, which is eated at one point by a Bunsen flame, arsenic in the amorhous condition is deposited upon the tube immediately beyond he heated spot. Even when greatly diluted with hydrogen this action takes place, and it therefore affords a delicate test for the resence of exceedingly small quantities of arsenic. This method

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* Extensive experiments on this subject by C. R. Sanger (*Proc. American cademy*) have led him to believe that volatile organic arsenical compounds e produced under these circumstances. No compound was isolated hower.

for the detection of arsenical compounds is known as *Marsh's test*, and may be carried out by means of the apparatus seen in Fig. 126. Hydrogen is generated in the two-necked bottle from zinc and dilute sulphuric acid (which are themselves free from arsenic), and the arsenic in the form of an oxygen or a haloid compound is introduced.* On igniting the issuing gas, and depressing a white porcelain capsule into the flame, black stains of amorphous arsenic are produced ; and if the tube be heated as shown in the figure, the arsenic is deposited as a black film. The corresponding antimony compound, SbH_3 (*q.v.*), gives rise to a similar deposit of metallic antimony, when treated in the same way ; but the arsenic deposit is readily distinguished by being easily soluble in a solution of calcium hypochlorite. Many metals, such as sodium or potassium, when heated in arsenic hydride, form alloys with the arsenic, and hydrogen is set at liberty ; while metallic oxides when similarly treated form metallic arsenides and water.

FIG. 126.

Arsenic hydride is slightly soluble in water, but the solution on exposure to air deposits arsenic.

When passed into a solution of silver nitrate, metallic silver is precipitated, and a solution of arsenious oxide (the hypothetical arsenious acid, H_3AsO_3) is obtained, thus—

$$AsH_3+6AgNO_3+3H_2O=3Ag_2+6HNO_3+H_3AsO_3.$$

When the gas is passed into copper sulphate solution, cuprous arsenide is precipitated—

$$2AsH_3+3CuSO_4=3H_2SO_4+As_2Cu_3.$$

Arsenic hydride is decomposed by the halogens with energy, forming the haloid compound of arsenic and the halogen acid—

$$AsH_3+3Cl_2=AsCl_3+3HCl.$$

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* When minute traces of arsenic have to be detected, as in food analyses, the material is introduced into the cathode compartment of a small specially constructed electrolytic cell (Thorpe) in which pure dilute sulphuric acid is electrolysed.

Solid Arsenic Hydride.—When arsenide of potassium or sodium is acted upon by water, a soft brown solid substance separates, which contains equal atomic proportions of arsenic and hydrogen. Its molecular weight is unknown; its composition is therefore expressed by the formula, $(AsH)_n$.

COMPOUNDS OF ARSENIC WITH THE HALOGENS.

The following compounds are known—

$$AsF_3;\quad AsCl_3;\quad AsBr_3;\quad AsI_3.$$

Two other compounds with iodine have been described containing the elements in the proportion represented by the formulæ, AsI_2 and As_2I_5, the molecular weights of which are unknown.

Arsenic Fluoride, AsF_3, molecular weight = 132, is formed when sodium fluoride is heated with arsenic chloride—

$$3NaF + AsCl_3 = 3NaCl + AsF_3.$$

It is best obtained by distilling a mixture of arsenious oxide, powdered fluor spar, and sulphuric acid in a leaden retort. The hydrofluoric acid generated by the action of the acid upon the calcium fluoride reacts upon the arsenious oxide, thus—

$$As_4O_6 + 12HF = 4AsF_3 + 6H_2O.$$

Properties.—Arsenic fluoride is a colourless fuming liquid, boiling at 60.4°. It is rapidly decomposed by water into arsenious oxide and hydrofluoric acid. On this account it forms painful wounds when brought into contact with the skin.

Arsenic Chloride, $AsCl_3$, molecular weight = 181.35, is obtained when arsenic burns in chlorine, or when chlorine is passed over fragments of arsenic in a tube.

It is also produced when either arsenic or arsenious sulphide is distilled with mercuric chloride—

$$2As + 6HgCl_2 = 3Hg_2Cl_2 + 2AsCl_3.$$
$$As_2S_3 + 3HgCl_2 = 3HgS \quad + 2AsCl_3.$$

It is readily prepared by the action of hydrochloric acid upon arsenious oxide; for which purpose sodium chloride, arsenious oxide, and sulphuric acid are gently heated together in a retort connected with a well-cooled receiver—

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$

Properties.—Arsenic chloride is a colourless, fuming, and somewhat oily liquid which boils at 130.2°, and is extremely poisonous. In the presence of excess of water, or when added to warm water, it is decomposed into arsenious oxide and hydrochloric acid. With a small quantity of water a solid crystalline arsenic chlorhydroxide is formed, $As(HO)_2Cl$—

$$AsCl_3 + 2H_2O = 2HCl + As(HO)_2Cl.$$

Arsenious Bromide, $AsBr_3$.—This compound is formed by the direct union of arsenic with bromine, and is prepared by adding powdered arsenic to a solution of bromine in carbon disulphide. On evaporation the compound is deposited in the form of colourless deliquescent crystals, which melt at 20° to 25° to a straw-coloured liquid.

Arsenious Iodide, AsI_3, is obtained by heating a mixture of arsenic and iodine. It is most conveniently prepared by digesting a saturated ethereal solution of iodine with powdered arsenic in a flask with a reflux condenser. On filtering and cooling, the iodide deposits in the form of lustrous red hexagonal crystals.

OXIDES AND OXYACIDS OF ARSENIC.

Two oxides of arsenic are known, both of which act as anhydrides—

Arsenious oxide	As_4O_6.
Arsenic oxide (arsenic pentoxide) . . .	As_2O_5.

No acid corresponding to arsenious oxide is known in the free state, although the arsenites constitute a class of stable salts.

Three arsenic acids, derived from arsenic pentoxide, are known, analogous in constitution to the three phosphoric acids, namely—

Ortho-arsenic acid . .	H_3AsO_4 or $AsO(HO)_3$.
Pyro-arsenic acid . . .	$H_4As_2O_7$ or $As_2O_3(HO)_4$.
Metarsenic acid . . .	$HAsO_3$ or $AsO_2(HO)$.

ARSENIOUS OXIDE.

Formula, As_4O_6. Molecular weight = 396.

Mode of Formation.—Arsenious oxide is formed when arsenic burns in air or in oxygen, or when arsenic minerals are roasted in a current of air. On a small scale it may be produced by burning arsenic in a hard glass tube in a stream of oxygen, and allowing e white fumes of arsenious oxide to pass into a glass cylinder (as own in Fig. 127), where the greater part condenses, while the rest led into a draught flue.

Arsenious oxide is obtained as a secondary product, in the etallurgical process of roasting arsenical ores of nickel, cobalt, ı, silver, and others, for the extraction of these metals. It also obtained as a principal product by roasting arsenical rites. The ore is heated either upon the hearth of a reverratory furnace, where it is raked over from time to time, or is introduced by means of a *hopper* into one end of a long clayed iron cylinder, placed at an incline of about 1 in 18, and caused wly to revolve about its longitudinal axis (Fig. 128). The lower d of this cylinder enters a furnace, the upper end is connected to series of brickwork flues. The ore is delivered into the upper d of the revolving cylinder, and as it gradually gravitates down

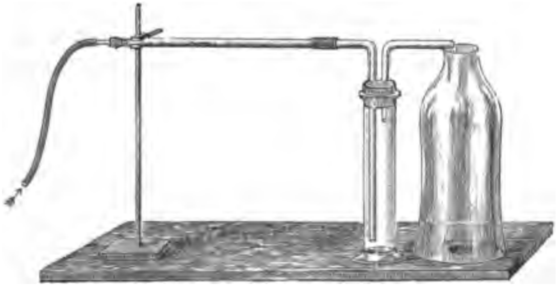

FIG. 127.

e incline, it is completely roasted by the furnace flames which ss over it, and finally falls out into a chamber beneath. The nes of arsenious oxide pass through a series of chambers or es, so arranged as to present an extensive condensing surface to e gases, and the crude product, known as *arsenical soot*, is from ne to time collected. This is known as Oxland and Hocking's volving calciner.

Properties.—Arsenious oxide, known familiarly as *white arsenic*, simply *arsenic*, is known in three modifications—

(1.) Amorphous.
(2.) Octahedral crystals of the cubic or regular system.
(3.) Prismatic crystals of the monosymmetric system.

Amorphous Arsenious Oxide is a colourless, transparent, vitreous substance, which is obtained when the vapour of the oxide is condensed at a temperature only slightly below its vaporising point. On exposure it gradually becomes opaque, being transformed into the regular octahedral variety. This change takes place from the outside, and lumps of opaque "white arsenic," when broken, often show a nucleus of the vitreous modification. Amorphous arsenious oxide may be preserved unchanged in sealed tubes. The change from the vitreous to the crystalline form is attended with evolution of heat, and a diminution of specific gravity from 3.738 to 3.689.

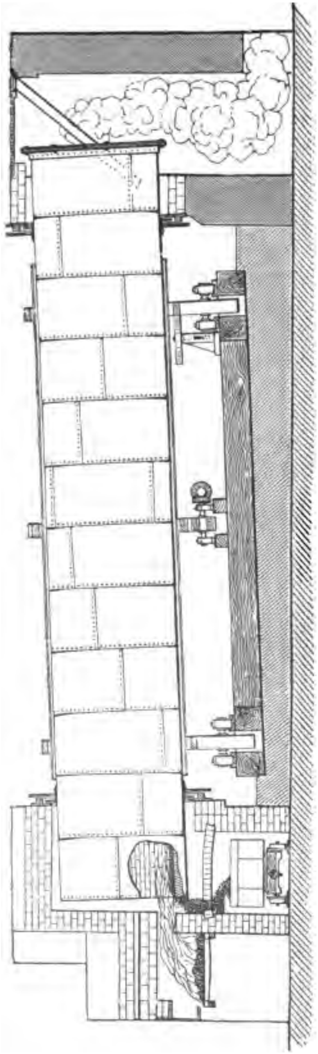

Fig. 128.

Amorphous arsenious oxide, when heated to about 200°, melts, and at a higher temperature vaporises. It is soluble in 108 parts of cold water.

Octahedral Arsenious Oxide.—The vitreous form passes spontaneously into this variety. It is obtained directly, by quickly cooling the vapour of arsenious oxide, or by crystallisation from the aqueous solution of either form of the oxide. Arsenious oxide is also deposited in this form from solution in hydrochloric acid.

Octahedral arsenious oxide is less soluble in water than the amorphous variety, 1 part requiring 355 parts of water for its lution. When heated, the crystals vaporise without fusion, but en heated under pressure they melt, and are converted into the treous form.

Prismatic Arsenious Oxide is obtained by crystallisation from a t saturated solution of arsenious oxide in potassium hydroxide.

Aqueous solutions of arsenious oxide possess a feeble acid re-tion, probably due to the formation of unstable arsenious acid, $_3AsO_3$. The acid has not been isolated, and on concentration e solution deposits crystals of arsenious oxide.

Arsenious oxide is a powerful poison : from 2 to 4 grains usually rove fatal. It is possible, however, by the habitual use of it, to accustom the system to this poison, that doses sufficiently large cause certain death to one unused to it may be taken with pparent impunity. The use of arsenic is said to beautify the omplexion, and to improve the wind. The men who are em-loyed upon arsenic works are constantly liable to swallow doses f arsenious oxide which would cause death to one unaccustomed the occupation.

Arsenites.—Three classes of arsenites are known, which may e regarded as being derived from the three hypothetical acids—

rtho-arsenious acid, H_3AsO_3, or $As(HO)_3$	Silver ortho-arsenite,	Ag_3AsO_3.
	Hydrogen copper arsenite (Scheele's green),	$HCuAsO_3$.
yro-arsenious acid, $H_4As_2O_5$, or $As_2O(HO)_4$	Calcium pyro-arsenite,	$Ca_2As_2O_5$.
	Barium pyro-arsenite,	$Ba_2As_2O_5$.
	Ammonium pyro-arsenite,	$(NH_4)_4As_2O_5$.
etarsenious acid, $HAsO_2$, or $AsO(HO)$	Potassium metarsenite,	$KAsO_2$.
	Acid potassium metarsenite,	$KAsO_2,HAsO_2$.
	Lead metarsenite,	$Pb(AsO_2)_2$.

The pigment known as *Schweinfurt green* is a double metar-enite and acetate of copper—

$$3Cu(AsO_2)_2,Cu(C_2H_3O_2)_2.$$

All arsenites, except those of the alkali metals, are insoluble in ater. When heated, most arsenites are converted into arsen*ates* nd arsenic ; and when heated with charcoal the whole of the rsenic is reduced.

Arsenic Pentoxide, As_2O_5.—This oxide is not formed when rsenic burns in oxygen. It is obtained by the oxidation of arsenious oxide by nitric acid, and subsequently heating the arsenic acid so produced, to a dark-red heat—

$$2H_3AsO_4=3H_2O+As_2O_5.$$

Properties.—Arsenic pentoxide is a white deliquescent solid, completely soluble in water, with the formation of arsenic acid.

When strongly heated it breaks up into arsenious oxide and oxygen—

$$2As_2O_5=As_4O_6+2O_2.$$

ARSENIC ACIDS AND ARSENATES.

When arsenic pentoxide is dissolved in water, crystals are obtained having the composition $2AsO(HO)_3,H_2O$. At 100° these melt and lose water, leaving ortho-arsenic acid, H_3AsO_4. By the withdrawal of water from this acid, both pyro- and metarsenic acid are obtained.

Heated between 140° and 180°, two molecules of the "ortho" acid lose one of water—

$$2H_3AsO_4=H_4As_2O_7+H_2O.$$

And by heating the pyro-arsenic acid so obtained to 200°, another molecule of water is expelled, with the formation of metarsenic acid (*compare corresponding acids of phosphorus*)—

$$H_4As_2O_7=2HAsO_3+H_2O.$$

Pyro- and metarsenic acids are both crystalline solids, which dissolve in water with the evolution of heat and formation of ortho-arsenic acid; aqueous solutions of these two acids, therefore, cannot exist. In this respect they differ from the corresponding phosphorus acids, both of which can be obtained in aqueous solution.

Each of the three arsenic acids forms salts, of which the following are examples:—

Trisodium ortho-arsenate . . .	Na_3AsO_4.
Hydrogen disodium ortho-arsenate .	HNa_2AsO_4.
Dihydrogen sodium ortho-arsenate .	H_2NaAsO_4.
Ammonium magnesium ortho-arsenate .	$(NH_4)MgAsO_4$.
Sodium pyro-arsenate	$Na_4As_2O_7$.
Sodium metarsenate	$NaAsO_3$.

The salts of pyro- and metarsenic acids, like the acids themelves, only exist in the solid state; when dissolved in water they ass into the ortho-compounds.

The arsenates are isomorphous with the corresponding phoshates.

COMPOUNDS OF ARSENIC WITH SULPHUR.

Three sulphides of arsenic are known, namely—

Arsenic disulphide (*found native as Realgar*) .	As_2S_2.
Arsenic trisulphide (*found native as Orpiment*) .	As_2S_3.
Arsenic pentasulphide	As_2S_5.

Arsenic Disulphide, As_2S_2, is formed when sulphur and arsenic, r arsenic trisulphide and arsenic, are heated together; or by eating arsenious oxide and sulphur—

$$As_4O_6+7S=2As_2S_2+3SO_2.$$

It is prepared on a large scale by distilling a mixture of iron yrites and arsenical pyrites—

$$FeS_2,FeAs_2+2FeS_2=As_2S_2+4FeS.$$

Properties.—Arsenic disulphide is a red, vitreous, brittle solid, aving a specific gravity of 3.5. It is readily fusible, and sublimes nchanged. Heated in air or oxygen, it burns with a blue flame, rming arsenious oxide and sulphur dioxide—

$$2As_2S_2+7O_2=4SO_2+As_4O_6.$$

Arsenic disulphide is employed in pyrotechny. So-called *Bengal re* consists of a mixture of realgar, sulphur, and nitre.

Arsenic Trisulphide, As_2S_3, is obtained by heating sulphur nd arsenic in the proportion required by the formula, and sublimng the compound.

It may readily be produced by passing sulphuretted hydrogen rough a solution of arsenious oxide in hydrochloric acid—

$$As_4O_6+6H_2S=2As_2S_3+6H_2O.$$

Properties.—The compound, as obtained by precipitation with ulphuretted hydrogen, is a pure canary-yellow solid, which easily melts, and on again cooling forms a brittle crystalline mass. It volatilises and sublimes unchanged, but when heated in air or oxygen it burns with formation of arsenious oxide and sulphur dioxide.

Arsenic trisulphide may be regarded as a thio-anhydride, as it gives rise to a series of salts known as *thio-arsenites*, or *sulpharsenites*. Thus, when arsenic trisulphide is brought into a solution of a caustic alkali, such as potassium hydroxide, the sulphide readily dissolves with the formation of an arsenite and thio-arsenite, thus—

$$As_2S_3 + 4KHO = HK_2AsO_3 + HK_2AsS_3 + H_2O.$$

Upon the addition of an acid, the salts are decomposed and arsenic trisulphide reprecipitated—

$$HK_2AsO_3 + HK_2AsS_3 + 4HCl = 4KCl + 3H_2O + As_2S_3.$$

Thio-arsenites.—These salts may be looked upon as being derived from three hypothetical thio-arsenious acids, corresponding to the oxyacids—

Ortho-thio-arsenious acid, H_3AsS_3.	Potassium ortho-thio-arsenite, K_3AsS_3.
Pyro-thio-arsenious acid, $H_4As_2S_5$.	Ammonium pyro-thio-arsenite, $(NH_4)_4As_2S_5$. Lead pyro-thio-arsenite, $Pb_2As_2S_5$.
Meta-thio-arsenious acid, $HAsS_2$.	Potassium meta-thio-arsenite, $KAsS_2$.

Thio-arsenites of the alkali metals, the metals of the alkaline earths, and of magnesium, are soluble in water, but decompose on boiling. Their solutions are decomposed by acids, with evolution of sulphuretted hydrogen and precipitation of arsenic trisulphide, thus—

$$2K_3AsS_3 + 6HCl = 6KCl + 3H_2S + As_2S_5.$$

Arsenic Pentasulphide, As_2S_5.—This compound is prepared by adding an acid to a solution of a thio-arsenate, thus—

$$2Na_3AsS_4 + 6HCl = 6NaCl + 3H_2S + As_2S_5.$$

Arsenic pentasulphide is a yellow, easily fusible solid. It is readily soluble in caustic alkalies, forming an arsenate and a thio-arsenate—

$$4As_2S_5 + 16KHO = 3HK_2AsO_4 + 5HK_2AsS_4 + 4H_2O.$$

Arsenic pentasulphide, like the trisulphide, gives rise to a series of salts, known as thio-arsenates. These may be regarded as being derived from the three hypothetical thio-arsenic acids—

Ortho-thio-arsenic acid, H_3AsS_4.	Tripotassium ortho-thio-arsenate, K_3AsS_4. Hydrogen disodium ortho-thio-arsenate, HNa_2AsS_4.
Pyro-thio-arsenic acid, $H_4As_2S_7$.	Magnesium pyro-thio-arsenate, $Mg_2As_2S_7$.
Meta-thio-arsenic acid, $HAsS_3$.	Ammonium meta-thio-arsenate $(NH_4)AsS_3$.

ANTIMONY.

Symbol, Sb. Atomic weight=120.

Occurrence.—Antimony in the uncombined state is found in small quantities in various parts of the world, and notably in Borneo. In combination with oxygen, as Sb_2O_3, it constitutes the mineral *antimony bloom*, or *white antimony;* and as Sb_2O_4 it occurs in *antimony ochre.* In combination with sulphur, as Sb_2S_3, it occurs as the mineral *stibnite*, or *grey antimony ore*, which is the most important source of the metal; and with both oxygen and sulphur, as $Sb_2O_3,2Sb_2S_3$, it constitutes the mineral *antimony blende*, or *red antimony.*

It also occurs in combination with sulphur and with metals, in the form of *thio-antimonites.*

Modes of Formation.—(1.) Antimony is obtained from the native sulphide by one of the two following methods. The broken-up ore is heated in plumbago crucibles along with scrap iron. As the mass melts, the sulphur combines with the iron, forming a slag of iron sulphide, and the liberated antimony settles out beneath—

$$Sb_2S_3+3Fe=2Sb+3FeS.$$

(2.) The crude sulphide is first *liquated*, or melted in such a manner as to separate the sulphide from the rocky matter associated with it. The liquated sulphide is then mixed with about half its weight of charcoal, in order to prevent the mass from caking, and carefully roasted. During this process the antimony sulphide is partially converted into antimony trioxide $(Sb_2O_3)_2$, which passes into flues, and is there condensed, leaving a mixture containing antimony tetroxide (Sb_2O_4), and unchanged sulphide. Most of the arsenic present is also oxidised, and volatilises with the antimony trioxide, while sulphur dioxide escapes. The residue, consisting of the tetroxide and sulphide (known as antimony ash) is mixed with an additional quantity of charcoal and with sodium carbonate, and heated to redness in a crucible, when the changes represented by the following equations take place—

$$(1.)\ Sb_2O_4+4C=4CO+2Sb.$$

By the action of the carbon upon the sodium carbonate, sodium is liberated, which combines with the sulphur of the trisulphide, forming sodium sulphide and metallic antimony—

$$(2.)\ Na_2CO_3+2C=3CO+2Na.$$
$$(3.)\ Sb_2S_3+6Na=3Na_2S+2Sb.$$

The sodium sulphide in its turn unites with a further quantity of antimony sulphide, forming a double sulphide of sodium and antimony, which, mixed with the sodium carbonate and charcoal, constitutes the slag. The metal obtained by either process is subsequently *refined.*

Properties.—Antimony is a bright, highly crystalline, and very brittle metal, possessing a bluish-white colour, and having a specific gravity of 6.7 to 6.8. It is unacted upon by air or oxygen at the ordinary temperature, but when heated it burns brilliantly, forming antimony trioxide. The metal melts at 450°; and when allowed to solidify, its crystalline character is seen by the fern-like appearance of its surface. If a quantity of the molten metal be allowed slowly to cool, and when partially solidified the remaining liquid portion be poured off, the interior of the mass is found to be lined with well-formed rhombohedral crystals, isomorphous with arsenic. In the act of solidification antimony expands, a property which it imparts to its alloys, thus giving to them the valuable quality of taking very fine and sharp castings. The most important of these alloys are *type metal* (lead 75, antimony 20, tin 5); *stereotype metal* (lead 112, antimony 18, tin 3); *Britannia metal* (tin 140, copper 3, antimony 9). Regarded as a metal, antimony is a bad conductor of heat and electricity.

Dilute sulphuric and hydrochloric acids are without action upon antimony. The concentrated acids convert it into sulphate and chloride respectively—

$$2Sb+6H_2SO_4=3SO_2+6H_2O+Sb_2(SO_4)_3.$$

Antimony is oxidised by nitric acid, dilute acid converting it into antimony trioxide or a compound of the oxide with nitrogen pentcxide, $Sb_2O_3,3N_2O_5$, while strong acid oxidises it chiefly into antimony tetroxide and pentoxide.

Powdered antimony, when thrown into chlorine, takes fire spontaneously and forms antimony trichloride.

Amorphous Antimony.—Antimony is obtained in an amorphous form by the electrolysis of a solution of tartar emetic in antimony trichloride.

Properties.—Amorphous antimony presents the appearance of smooth polished rod of graphite, and has a specific gravity of .78. It always contains a certain quantity of antimony trichloride rom 4 to 12 per cent.); but whether this is in chemical union or erely mechanically retained by the metal is not known. Amorhous antimony is very unstable, and readily passes into the rystalline modification; a slight blow, even a scratch with a eedle, causes it instantly to transform itself into the stable form ith explosive violence, the temperature at the same moment ising to 250°, and clouds of the vapour of antimony trichloride eing evolved.

ANTIMONY HYDRIDE (*Antimoniuretted Hydrogen*).

Symbol, SbH_3.

Modes of Formation.—(1.) This compound has never been btained in the pure state—as usually prepared it is always mixed vith hydrogen. It is formed when a solution of antimony trihloride in hydrochloric acid is introduced into a mixture generating ydrogen, such as zinc and sulphuric acid.

(2.) It is also found by the action of dilute sulphuric acid upon lloys of antimony and zinc—

$$Sb_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2SbH_3.$$

Properties.—Antimony hydride is a colourless, offensive-smellng, and poisonous gas, closely resembling the corresponding rsenic compound in its general behaviour. It burns with a violetinted flame, forming water and antimony trioxide—

$$4SbH_3 + 6O_2 = 6H_2O + Sb_4O_6.$$

When the supply of air is limited water is formed and antimony s deposited; when, therefore, a cold object is depressed upon the flame black stains of metallic antimony are obtained. The gas is easily decomposed by heat, and if passed through a glass tube heated at one point a black deposit of antimony is formed upon he glass. The antimony so deposited is insoluble in a solution of bleaching powder (see Arsenic Hydride). Antimony hydride is decomposed by the halogen elements, with the formation of the halogen hydride, and the halogen compound of antimony—

$$SbH_3 + 3Cl_2 = 3HCl + SbCl_3$$

Sulphuretted hydrogen, under the influence of sunshine, converts antimony hydride into antimony trisulphide—

$$2SbH_3+3H_2S=Sb_2S_3+6H_2.$$

When passed into silver nitrate solution the antimony is precipitated in combination with silver, in this way differing from the arsenic analogue—

$$SbH_3+3AgNO_3=3HNO_3+SbAg_3.$$

COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

The compounds represented by the following formulæ are known—

$$SbF_3\ ;\ SbCl_3\ ;\ SbBr_3\ ;\ SbI_3$$
$$SbF_5\ ;\ SbCl_5.$$

Antimony Trifluoride, SbF_3, is prepared by dissolving the trioxide in aqueous hydrofluoric acid. From the concentrated solution it is deposited in the form of white deliquescent crystals. It dissolves in water, and is gradually converted into an oxyfluoride.

Antimony Pentafluoride, SbF_5, is obtained when hydrated antimony pentoxide is dissolved in aqueous hydrofluoric acid. When the solution is evaporated the compound remains as an amorphous gum-like residue.

Both of these fluorides exhibit a great tendency to unite with alkaline fluorides, forming double salts, such as $SbF_3,2KF$; $SbF_3,2NH_4F$, in the case of the trifluoride ; and SbF_5,KF ; $SbF_5,2KF$, with the pentafluoride.

Antimony Trichloride, $SbCl_3$, is formed when chlorine is passed over metallic antimony, or antimony trisulphide—

$$2Sb+3Cl_2=2SbCl_3.$$
$$2Sb_2S_3+9Cl_2=4SbCl_3+3S_2Cl_2.$$

It may also be obtained by the action of boiling hydrochloric acid, containing a small quantity of nitric acid, upon either metallic antimony, antimony trioxide, or trisulphide—

$$Sb_2S_3+6HCl=2SbCl_3+3H_2S.$$

Properties.—Antimony trichloride is a colourless, deliquescent, crystalline substance, melting at 73.2° to an oily liquid, which again solidifies to a soft translucent mass. It is soluble in alcohol and in carbon disulphide, and from the latter may be crystallised. It may be dissolved in a small quantity of water unchanged. Thus, allowed to deliquesce it liquefies in the water it absorbs, forming colourless solution, which, upon evaporation over sulphuric acid, gain deposits crystals of the trichloride. The addition of larger uantities of water results in the formation of oxychlorides *—

$$
\begin{aligned}
&(1.)\quad SbCl_3 + H_2O = 2HCl + SbOCl.\\
&(2.)\quad 4SbCl_3 + 5H_2O = 10HCl + Sb_4O_5Cl_2.
\end{aligned}
$$

Continued boiling with water removes the whole of the chlorine, orming the trioxide—

$$Sb_4O_5Cl_2 + H_2O = 2HCl + Sb_4O_6.$$

Antimony chloride unites with alkaline chlorides, forming double salts (see Antimony Fluoride), such as $SbCl_3,2NH_4Cl$; $SbCl_3,3KCl$. With potassium bromide it forms the compound $SbCl_3,3KBr$, which, strangely enough, appears o be identical with the double compound of antimony tribromide with potassium chloride, $SbBr_3,3KCl$.

Antimony Pentachloride, $SbCl_5$, is obtained by passing excess of dry chlorine over metallic antimony, or antimony trichloride, in a retort, when antimony pentachloride distils over in the excess of chlorine—

$$SbCl_3 + Cl_2 = SbCl_5.$$

Properties.—Antimony pentachloride is a nearly colourless, strongly-fuming liquid. It solidifies, when cooled, to a mass of colourless crystals, which remelt at −6°. Under the ordinary atmospheric pressure the pentachloride dissociates, when heated, into the trichloride and chlorine, but under reduced pressure it may be boiled and distilled. Thus, under a pressure of 22 mm. it boils at 79°.

By the regulated action of ice-cold water, oxychlorides are formed—

$$
\begin{aligned}
&(1.)\quad SbCl_5 + H_2O = SbOCl_3 + 2HCl.\\
&(2.)\quad SbOCl_3 + H_2O = SbO_2Cl + 2HCl.
\end{aligned}
$$

Antimony pentachloride, and also the oxychlorides, are converted by hot water into pyro-antimonic acid (analogous to pyro-arsenic and pyro-phosphoric acids)—

$$
\begin{aligned}
2SbCl_5 + 7H_2O &= H_4Sb_2O_7 + 10HCl.\\
2SbO_2Cl + 3H_2O &= H_4Sb_2O_7 + 2HCl.
\end{aligned}
$$

---

* The mixed product obtained by the action of water upon antimony trichloride is known as *powder of Algaroth.*

Sulphuretted hydrogen (the sulphur analogue of water) acts upon antimony pentachloride, forming antimony sulphotrichloride, corresponding to the oxytrichloride—

$$SbCl_5 + H_2S = SbSCl_3 + 2HCl.$$

Antimony tribromide, $SbBr_3$, and antimony tri-iodide, SbI_3, are obtained by adding powdered antimony to solutions of the halogens in carbon disulphide, from which liquid the compounds are crystallised: the bromide as colourless deliquescent crystals, and the iodide as hexagonal ruby-red crystals. Both of these compounds are similarly acted upon by water, forming the oxybromides $SbOBr$; $Sb_4O_5Br_2$, and the oxyiodides $SbOI$; $Sb_4O_5I_2$.

OXIDES AND OXYACIDS OF ANTIMONY.

Three oxides of antimony are known—

Antimony trioxide (antimonious oxide) .	$(Sb_2O_3)_2$ or Sb_4O_6.
Antimony tetroxide	Sb_2O_4.
Antimony pentoxide	Sb_2O_5.

No acids are known corresponding to the trioxide, although a sodium salt of the hypothetical metantimonious acid, $HSbO_2$, has been described, having the composition $NaSbO_2,3H_2O$.

Three acids are known derived from antimony pentoxide which are analogous to the three arsenic and phosphoric acids—

Orthoantimonic acid	H_3SbO_4.
Pyroantimonic acid	$H_4Sb_2O_7$.
Metantimonic acid	$HSbO_3$.

Antimony Trioxide, Sb_4O_6, may be prepared by the addition of hot water to a solution of either antimony trichloride or antimony sulphate, and washing the precipitated oxide with a solution of sodium carbonate to remove the free acid—

$$4SbCl_3 + 6H_2O = Sb_4O_6 + 12HCl.$$

Properties.—Antimonious oxide is a white powder, which, when volatilised, condenses in two distinct forms, namely, prismatic crystals of the trimetric system and regular octahedra. The former are deposited nearest to the heated material, the latter in more remote and cooler regions. (See *Arsenious Oxide, with which antimonious oxide is isodimorphous.*) Antimonious oxide is only very slightly soluble in water, and the solution is without tion upon litmus. It is insoluble in nitric or sulphuric acid, but dissolved by hydrochloric acid with formation of the trichloride. is readily soluble in tartaric acid, and in a boiling solution hydrogen potassium tartrate (*cream of tartar*), giving rise to otassium antimony tartrate, or *tartar emetic*—

$$4HK(C_4H_4O_6) + Sb_4O_6 = 4(SbO)K(C_4H_4O_6) + 2H_2O.$$

Antimonious oxide burns in the air, forming the tetroxide—

$$(Sb_2O_3)_2 + O_2 = 2Sb_2O_4.$$

Antimony Tetroxide, Sb_2O_4, is formed when the trioxide burns n air. It may be prepared by strongly heating antimony pentxide—

$$2Sb_2O_5 = 2Sb_2O_4 + O_2.$$

Properties.—Antimony tetroxide is a white non-volatile powder hich is insoluble in water. It is decomposed by boiling hydrogen otassium tartrate, forming tartar emetic and metantimonic acid, hus—

$$HK(C_4H_4O_6) + Sb_2O_4 = (SbO)K(C_4H_4O_6) + HSbO_3.$$

Antimony Pentoxide, Sb_2O_5, is obtained by oxidising metallic ntimony with nitric acid, and heating the antimonic acid so btained to a temperature not exceeding 275°.

Properties.—Antimony pentoxide is a straw-coloured powder, nsoluble in water. When heated to 300° it gives up oxygen and converted into the tetroxide. Its feeble acidic character is seen y its formation of an alkaline metantimonate when fused with an lkaline carbonate—

$$Sb_2O_5 + Na_2CO_3 = CO_2 + 2NaSbO_3.$$

Antimonic Acids and Antimonates.—None of the three antimonic acids n be obtained by the action of water upon the oxide. Pyro-antimonic acid formed when antimony pentachloride is treated with hot water, and the recipitate dried at 100°—

$$2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl.$$

Pyro-antimonic acid readily passes, by loss of water. into metantimonic cid—

$$H_4Sb_2O_7 - H_2O = 2HSbO_3.$$

Metantimonic acid is also formed by oxidising metallic antimony by means f nitric acid—

$$2Sb + 4HNO_3 = 2HSbO_3 + NO_2 + 3NO + H_2O,$$

or by the decomposition of an aqueous solution of a metantimonate by means of nitric acid—

$$KSbO_3+HNO_3=KNO_3+HSbO_3.$$

On allowing the precipitated metantimonic acid to remain for a long time in contact with water it is converted into ortho-antimonic acid, H_3SbO_4—

$$HSbO_3+H_2O=H_3SbO_4.$$

No salts of ortho-antimonic acid, H_3SbO_4, are known; the antimonates, therefore, belong to the two acids, pyro-antimonic acid and metantimonic acid—

Pyro-antimonates.*	Metantimonates.*
Normal potassium pyro-antimonate, $K_4Sb_2O_7$.	Potassium metantimonate, $KSbO_3$.
Hydrogen potassium pyro-antimonate, $H_2K_2Sb_2O_7$.	Barium metantimonate, $Ba(SbO_3)_2$.

COMPOUNDS OF ANTIMONY WITH SULPHUR.

Two sulphides of antimony are known, namely—

Antimony trisulphide	Sb_2S_3.
Antimony pentasulphide . . .	Sb_2S_5.

Antimony Trisulphide, Sb_2S_3.—This compound occurs native as the mineral *stibnite*, or *grey antimony ore.* It is prepared by heating a mixture of powdered antimony and sulphur (in proportion required by the formula) beneath a layer of fused sodium chloride in a crucible. It is also formed when sulphuretted hydrogen is passed through a solution of antimony trichloride, or a solution of tartar emetic—

$$2SbCl_3+3H_2S=Sb_2S_3+6HCl.$$

Properties.—Antimony trisulphide as it occurs native, and as obtained by the direct union of antimony and sulphur, is a grey-

---

* As only two types of antimonates are known, and as the salts of the type $MSbO_3$ are the best known, the name *antimonates* was formerly applied to them, and the term *metantimonates* was given to the salts belonging to the other class. It is better, however, to adopt the same system of nomenclature for the antimony compounds as that which is in use for the similarly constituted arsenic and phosphorus compounds—

	Phosphates.	Arsenates.	Antimonates.
Ortho . . .	M_3PO_4	M_3AsO_4	—
Pyro . . .	$M_4P_2O_7$	$M_4As_2O_7$	$M_4Sb_2O_7$
Meta . . .	MPO_3	$MAsO_3$	$MSbO_3$

black crystalline substance; as prepared by precipitation with sulphuretted hydrogen, and subsequently drying at 200°, it is a brick-red amorphous powder, which, when melted and slowly cooled, solidifies in the crystalline form. Antimony sulphide sublimes unchanged when heated in an inert gas, but when heated in air sulphur dioxide is evolved, and antimonious oxide and tetroxide are formed. Heated with hydrochloric acid, it evolves sulphuretted hydrogen, and forms antimony trichloride—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Antimony Pentasulphide, Sb_2S_5, is obtained when antimony pentachloride is mixed with water, and sulphuretted hydrogen passed through the liquid—

$$2SbCl_5 + 5H_2S = Sb_2S_5 + 10HCl,$$

or—

$$2SbO_2Cl + 5H_2S = Sb_2S_5 + 4H_2O + 2HCl.$$

Properties.—Antimony pentasulphide is a dark, orange-red powder, which, on being heated, is decomposed into the trisulphide and free sulphur.

Both of these antimony sulphides may be regarded as thio-anhydrides, for although no thio-acids derived from them are known, salts have been produced which may be viewed as derivatives of hypothetical thio-acids. When the trisulphide is either fused with caustic potash, or boiled in an aqueous solution, potassium thio-antimonite is formed—

$$2Sb_2S_3 + 4KHO = 3KSbS_2 + KSbO_2 + 2H_2O.$$

Similarly, when antimony pentasulphide is dissolved in potassium hydroxide, a mixture of antimonate and thio-antimonate is obtained—

$$4Sb_2S_5 + 24KHO = 5K_3SbS_4 + 3K_3SbO_4 + 12H_2O.$$

The following are illustrations of the thio-salts of antimony—

Sulphide.	Hypothetical Acids.	Salts.
Sb_2S_3 .	(Ortho) H_3SbS_3.	Potassium thio-antimonite, K_3SbS_3.
	(Meta) $HSbS_2$.	Silver thio-antimonite, $AgSbS_2$.
	(Pyro) $H_4Sb_2S_5$.	Lead thio-antimonite, $Pb_2Sb_2S_5$.
Sb_2S_5 . .	(Ortho) H_3SbS_4.	Potassium thio-antimonate, K_3SbS_4.
		Sodium thio-antimonate (Schlippe's salt) Na_3SbS_4.
		Barium thio-antimonate, $Ba_3(SbS_4)_2$.

Only ortho-thio-antimon*ates* are known.

BISMUTH.

Symbol, Bi. Atomic weight=208.5.

Occurrence.—Bismuth occurs most commonly in the uncombined condition. It is met with in combination with oxygen, as Bi_2O_3, in *bismuth ochre;* and in combination with sulphur, as Bi_2S_3, in *bismuth glance.*

Mode of Formation.—Bismuth is principally obtained from the native metal, and from ores with which metallic bismuth is associated. The broken-up ore is liquated by being heated in inclined iron pipes, when the bismuth readily melts and drains away.

Pure bismuth can be prepared from the crude metal thus obtained, by first dissolving it in nitric acid, forming bismuth nitrate $Bi(NO_3)_3$, and then precipitating the basic nitrate by the addition of water—

$$Bi(NO_3)_3 + 2H_2O = (BiO)NO_3,H_2O + 2HNO_3.$$

The basic nitrate is next dried and heated in a crucible with charcoal; the salt is first converted into the trioxide by the action of heat, and the oxide is then reduced by the carbon—

$$2(BiO)NO_3,H_2O = Bi_2O_3 + N_2O_4 + O + 2H_2O.$$
$$Bi_2O_3 + 3C = 3CO + 2Bi.$$

Properties.—Bismuth is a lustrous white metal with a faint reddish tinge. It melts at 268.3°. If the molten metal be allowed to cool until partially solidified, and the remaining liquid be then poured off, obtuse rhombohedral crystals (belonging to the hexagonal system), closely approaching to the cube, are obtained.

The specific gravity of bismuth is 9.823; it is extremely brittle, and a poor conductor of electricity. Bismuth is unacted upon by dry air at ordinary temperatures; moist air tarnishes its surface. Heated in air or oxygen it burns, forming the trioxide. It is only slightly attacked by hydrochloric acid, but is converted by hot sulphuric acid into a basic sulphate.

Bismuth readily forms alloys with other metals, and imparts to them the useful properties of ready fusibility and hardness. The alloys known by the general name of *fusible metal* contain bismuth; thus, *Wood's fusible metal*, which melts at 65°, consists of 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium.

COMPOUNDS OF BISMUTH WITH THE HALOGENS.

Compounds represented by the following formulæ are known—

BiF_3	$BiCl_3$	$BiBr_3$	BiI_3.
—	$(BiCl_2)_2$	$(BiBr_2)_2$?	—

Bismuth Trichloride, $BiCl_3$, may be prepared by passing dry chlorine over powdered bismuth gently heated in a retort. A yellow liquid is first formed, after which the stream of chlorine is stopped and the liquid distilled, when the trichloride sublimes in the form of crystals. It may also be obtained by distilling a mixture of powdered bismuth and mercuric chloride—

$$2Bi + 6HgCl_2 = 3Hg_2Cl_2 + 2BiCl_3.$$

Properties.—Bismuth trichloride is a white, extremely deliquescent crystalline compound. Heated in an atmosphere of chlorine, it melts to a yellow liquid. It is decomposed by water with the precipitation of bismuth oxychloride—

$$BiCl_3 + H_2O = 2HCl + BiOCl.$$

Bismuth Dichloride $(BiCl_2)_2$, is obtained by the prolonged heating of mercurous chloride and finely powdered bismuth to 230° in a sealed tube. The mixture melts, and mercury collects at the bottom, and on cooling the dichloride solidifies as a black, extremely deliquescent solid upon the surface of the mercury. When heated above 300° the dichloride is resolved into the trichloride and metallic bismuth. The molecular weight of the compound is unknown.

Bismuth Tribromide, $BiBr_3$, is prepared by gradually adding bromine to powdered bismuth and slightly warming the mixture for some time. The bromide sublimes in the form of golden-yellow, deliquescent crystals, which are decomposed by water, forming oxybromide, BiOBr.

Bismuth Tri-iodide, BiI_3, is prepared by subliming a mixture of iodine and bismuth. The sublimate is afterwards finely powdered and again sublimed, and the product finally distilled in a stream of carbon dioxide, when it forms dark grey crystals with a bright metallic lustre. Boiling water decomposes the compound, with formation of bismuth oxyiodide, BiOI.

COMPOUNDS OF BISMUTH WITH OXYGEN.

Four oxides of bismuth are known, namely—

Bismuth dioxide (*Hypobismuthous oxide*) . .	Bi_2O_2.
„ trioxide (*Bismuthous oxide*) . .	Bi_2O_3.
„ tetroxide (*Hypobismuthic oxide*) . .	Bi_2O_4.
„ pentoxide (*Bismuthic oxide*) . .	Bi_2O_5.

None of these compounds is an acid-forming oxide, although, with the exception of the first, they all form hydrated oxides. These hydrated oxides have no acidic properties, and no salts have been obtained in which the acidic or negative portion of the molecule consists of bismuth and oxygen. All the four oxides, when acted upon by acids, yield the same series of salts in which the bismuth fulfils the functions of a trivalent element, replacing three atoms of hydrogen. In the case of the dioxide, metallic bismuth is deposited, thus—

$$3Bi_2O_2 + 6H_2SO_4 = 2Bi_2(SO_4)_3 + 2Bi + 6H_2O.$$

While with the higher oxides oxygen is evolved—

$$Bi_2O_5 + 6HNO_3 = 2Bi(NO_3)_3 + 2O + 3H_2O.$$

Bismuth trioxide is the most stable and the most important of the oxides; when heated in air, the remaining three compounds are converted into the trioxide: the dioxide by oxidation, and the tetroxide and pentoxide by loss of oxygen. The trioxide alone is unchanged on being heated in air or oxygen.

Bismuth Dioxide, Bi_2O_2.—This oxide is prepared by adding a mixed solution of bismuth trichloride and stannous chloride to an excess of a 10 per cent. solution of caustic potash, air being excluded: potassium stannate is formed, and bismuth dioxide is precipitated—

$$SnCl_2 + 2BiCl_3 + 10KHO = Bi_2O_2 + 8KCl + K_2SnO_3 + 5H_2O.$$

Properties.—The precipitated compound, after being washed in dilute caustic potash and dried in vacuo, is obtained as a black crystalline powder. When heated in air it smoulders, uniting with oxygen to form the trioxide. When moist it oxidises spontaneously—

$$Bi_2O_2 + O = Bi_2O_3.$$

Bismuth Trioxide, Bi_2O_3, is formed when the metal is burnt in air or oxygen. It may also be obtained by heating the hydrated oxides, the carbonate, or basic nitrate, thus—

$$Bi_2O_3,H_2O = Bi_2O_3 + H_2O.$$
$$Bi_2O_3,CO_2 = Bi_2O_3 + CO_2.$$
$$2(BiO)NO_3,H_2O = Bi_2O_3 + 2NO_2 + O + 2H_2O.$$

Properties.—Bismuth trioxide is a cream-coloured powder, insoluble in and unacted upon by water, and is the only oxide of bismuth which is unchanged when heated in the air or in oxygen. It dissolves in acids, forming salts of bismuth—

$$Bi_2O_3+6HNO_3=3H_2O+2Bi(NO_3)_3.$$
$$Bi_2O_3+3H_2SO_4=3H_2O+Bi_2(SO_4)_3.$$

With small quantities of hydrochloric acid it first forms bismuth oxychloride, BiOCl, which dissolves in additional acid, yielding the trichloride—

$$Bi_2O_3 + 2HCl=H_2O+2BiOCl.$$
$$BiOCl+2HCl=H_2O+BiCl_3.$$

None of these compounds is soluble in water without the presence of excess of the acid. Water alone converts them into insoluble basic salts and free acid, which in the state of extreme dilution is unable to exert any solvent action. Thus, in the case of the nitrate when water is added, this compound is decomposed into the basic nitrate and free nitric acid—

$$Bi(NO_3)_3+2H_2O=(BiO)NO_3,H_2O+2HNO_3.$$

Bismuth trioxide forms three hydrates, represented by the formulæ—

$$Bi_2O_3,H_2O. \qquad Bi_2O_3,2H_2O. \qquad Bi_2O_3,3H_2O.$$

These hydrates have no acid properties, and are incapable of combining with bases to form salts, but themselves play the part of a base, uniting with acids to form bismuth salts.

The trihydrate is obtained by pouring an acid solution of bismuth nitrate into an excess of strong aqueous ammonia—

$$2Bi(NO_3)_3+6NH_3H_2O=6NH_4(NO_3)+Bi_2O_3,3H_2O.$$

Heated to 100° it is converted by loss of water into the monohydrate—

$$Bi_2O_3,3H_2O=Bi_2O_3,H_2O+2H_2O.$$

Bismuth Tetroxide, Bi_2O_4, is formed by the action of potassium hypochlorite upon the trioxide, the product being dried at 180°—

$$Bi_2O_3+KClO=Bi_2O_4+KCl.$$

Properties.—Bismuth tetroxide is a brownish-yellow powder, which readily parts with an atom of oxygen and passes into the trioxide.

Bismuth Pentoxide, Bi_2O_5, is prepared by passing chlorine into a nearly boiling solution of caustic potash in which is suspended a quantity of bismuth trioxide—

$$Bi_2O_3+4KHO+2Cl_2=4KCl+H_2O+Bi_2O_5,H_2O.$$

Properties.—Bismuth pentoxide is a red powder, which is readily deoxidised into the tetroxide and trioxide by heat. It combines with water, forming the hydrate Bi_2O_5,H_2O, but with excess of water it is gradually deoxidised into hydrates of the tetroxide or trioxide.

Bismuth pentoxide is reduced, with evolution of oxygen, by both nitric and sulphuric acids—

$$Bi_2O_5+3H_2SO_4=Bi_2(SO_4)_3+3H_2O+O_2.$$

With hydrochloric acid it behaves in the usual manner of peroxides, causing the evolution of chlorine—

$$Bi_2O_5+10HCl=2BiCl_3+5H_2O+Cl_2.$$

Bismuth Trisulphide, Bi_2S_3.—This compound is the only compound of bismuth with sulphur that is known with certainty. It occurs native as the mineral *bismuth glance.*

It is precipitated when sulphuretted hydrogen is passed into a solution of a bismuth salt—

$$2Bi(NO_3)_3+3H_2S=Bi_2S_3+6HNO_3.$$

It is also obtained by heating together the requisite proportions of bismuth and sulphur.

Properties.—As obtained by precipitation, bismuth sulphide is a dark brown, almost black powder; the native sulphide forms steel-grey lustrous crystals.

It is decomposed, when strongly heated, into its constituent elements. Bismuth sulphide differs from the corresponding antimony and arsenic compound in not being dissolved by alkaline hydrates or sulphides.

CHAPTER IV

THE ELEMENTS OF GROUP I. (FAMILY A.)

THIS family comprises the following five elements, known as the *alkali metals*—

	Atomic Weights.	Melting-points.
Lithium (Li)	7.03	180°
Sodium (Na)	23.05	95.6°
Potassium (K)	39.15	62.5°
Rubidium (Rb)	85.5	38.5°
Caesium (Cs)	132.9	26.5°

The most important and the most abundant of these elements are potassium and sodium, which also were the first to be discovered, having been isolated by Davy in the year 1807. The element lithium, although widely distributed in nature, is for the most part found only in minute quantities; the element was first isolated by Bunsen in the year 1855. The two remaining elements are still rarer substances, usually met with in very minute quantities accompanying sodium and potassium. Both of these elements were discovered by Bunsen by means of the spectroscope—caesium in 1860 and rubidium in the following year.

All these elements are soft, silvery-white metals, which may be readily cut with a knife, and which rapidly tarnish in the air. They all decompose water at the ordinary temperature. The members of this family exhibit that gradation in properties which is met with in all similar families. Thus, their melting-points gradually decrease as their atomic weights rise, as will be seen from the figures given above. Their chemical activity also steadily increases as we pass from lithium to caesium. Thus, in the case of their behaviour in contact with water: potassium, when thrown upon cold water, decomposes that liquid with sufficient energy to cause the ignition of the hydrogen which is evolved; sodium under the same conditions melts and floats about upon the surface, but the action is not sufficiently energetic to effect the inflammation of the gas, unless the water be previously heated; while with lithium, even with boiling water, the temperature produced by the reaction does not rise to the ignition-point of hydrogen. The same is also seen in the spontaneous oxidation of these elements when they are exposed to the air. Thus, lithium when cut with a knife, although it is soon covered with a film of oxide, nevertheless retains its bright metallic surface for some seconds; sodium tarnishes so much more quickly, that the film of oxide appears almost to follow the knife. When potassium is cut the bright surface can scarcely be seen, so rapid is the oxidation, and if left exposed a fragment of the metal soon begins to melt by the heat of its own oxidation, and frequently spontaneously ignites. With rubidium and caesium the oxidation is even more rapid, and a fragment of these metals freely exposed to the air very rapidly takes fire spontaneously.

The electro-positive character of these elements gradually increases from lithium to caesium, which is the most electro-positive of all the known elements.

The term *alkali*, applied to metals of this family, was originally used (before any distinction was made between potash and soda) to denote the salt obtained by treating the ashes of plants with water. Later on, in order to distinguish between this substance and what became known as the *volatile alkali* (*i.e.* ammonium carbonate), it was termed the *fixed alkali*. The first distinction between potash and soda was based upon the erroneous belief that the former was entirely of vegetable origin, while the latter was only to be found in the mineral kingdom; hence the names *vegetable alkali* and *mineral alkali* were used to denote these two substances, both of which were regarded as elementary bodies until 1807, when Davy showed that they contained the two metals potassium and sodium.

The resemblance between the different members of this family and between their compounds is very close; so much so, that in the case of sodium, potassium, rubidium, and caesium, there are scarcely any ordinary chemical reactions by which they can be distinguished. They are all readily identified, however, by means of the spectroscope. When a minute quantity of a lithium salt is introduced upon a loop of platinum wire into the non-luminous Bunsen flame, the latter is tinged a brilliant crimson-red colour; a potassium salt similarly treated colours the flame a delicate lilac, while a sodium compound gives a brilliant daffodil-yellow colour. The colour imparted to a flame by rubidium and caesium salts is indistinguishable by the eye from that given by potassium compounds; and, moreover, when any of these are mixed with a sodium salt the intense yellow emitted by the latter completely masks the colours given by the others. By means of the spectroscope, not only are the apparently similar colours given by potassium, rubidium, and

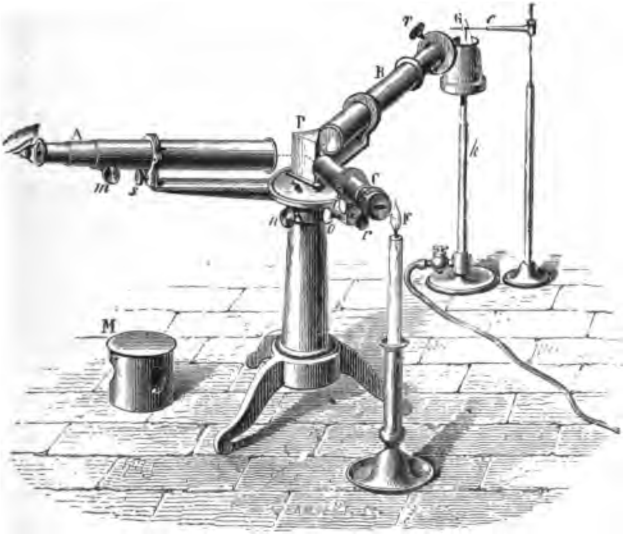

FIG. 129.

caesium readily distinguished, but the presence of any or all of them is easily detected, even when admixed with sodium salts. Spectrum analysis is based upon the fact that light of different colours has different degrees of refrangibility, and therefore when passed through a prism the different coloured rays are bent out of their straight course at different angles. Ordinary white light is composed of rays of all degrees of refrangibility, *i.e.* rays of all colours; hence, when a beam of such light is passed through a prism, the various coloured rays are separated and become spread out in the order of their refrangibility, from the least refrangible red at the one extreme to the deep violet at the other. This familiar "rainbow" coloured band of light is termed the *continuous spectrum*.

A simple form of spectroscope is seen in Fig. 129. The light is caused to pass through a narrow slit at the end of the fixed tube B, known as the collimator tube. If the prism P be removed and the telescope A be moved round so as to be in a continuous line with B, a magnified image of the slit is seen by the observer. When the prism is replaced, and A is moved into such a position that the bent rays fall upon its lens, the continuous spectrum is seen, which is an infinite number of strips of light (corresponding to the image of the slit) of all colours arranged side by side. If the light to be examined, instead of being ordinary white light, were composed of rays all of one degree of infrangibility (*i.e.* monochromatic light), there would be produced only a single image of the slit, which would fall in that position corresponding to the particular degree of refrangibility of the light. Such a monochromatic light is produced when a sodium salt is heated in a Bunsen flame; if, therefore, a salt of this metal be introduced upon a loop of platinum wire into the non-luminous flame G, and the light, after passing through the prism, be observed through A, instead of a continuous spectrum, there will be seen a single image of the slit, falling in the brightest yellow part of the spectrum. When the sodium salt is replaced by a lithium salt, it is seen that two images of the slit are obtained, one in the red and the other in the yellow regions of the spectrum. The light emitted from this element consists of rays of two degrees of refrangibility. We say, therefore, that the spectrum of sodium is one yellow *line*,* and that of lithium consists of one red and one yellow *line*. In order to distinguish the positions of, for example, the yellow lithium line and that given by sodium, an image of a graduated scale, illuminated by the candle flame F, is also thrown into the telescope A.

If salts of sodium and lithium mixed together be introduced into the flame G, then three images of the slit are seen, namely, the yellow line given by the sodium, the yellow line of the lithium, situated slightly nearer the red, and the lithium red line.

Potassium, like lithium, gives a light of two degrees of refrangibility, forming consequently two images of the slit, one in the deep red and the other in the deep violet; if, therefore, lithium, sodium, and potassium salts are mixed, and examined by the spectroscope, five lines are seen (Fig. 130), namely, two red (one belonging to lithium and one to potassium), two yellow (one belonging to lithium and one to sodium), and the violet line of potassium.

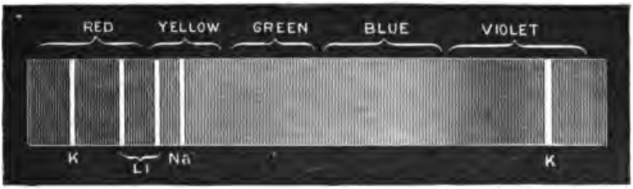

FIG. 130.

When analysed in this manner, the lights emitted by rubidium and caesium compounds are seen to be totally different from each other, and from potassium. The spectrum of rubidium consists of two prominent lines in the violet (nearer the blue region than that belonging to potassium), two brilliant red lines (very near the potassium red line), and a number of less brilliant lines in the

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* In reality, when examined by a higher dispersive power, the sodium line is seen to be a group of lines.

orange, yellow, and green. That of caesium consists of two brilliant blue lines, two bright red lines (near the lithium red line), and a number of less prominent lines in the yellow and green. It will be seen, therefore, that the three elements potassium, rubidium, and caesium may be at once sharply distinguished by this optical method of analysis, although they so closely resemble one another in their chemical behaviour, as to render it highly probable that the separate existence of the two latter would never have been discovered by chemical methods alone.

Indeed, before the discovery of caesium by Bunsen, a rare mineral known as *Pollux* (now known to contain caesium) was mistaken for a potassium mineral.*

The element lithium, the member of the family that belongs to the *Typical series*, exhibits certain characteristic differences from the other members. This is seen particularly in the case of the carbonate and phosphate of this element. Lithium carbonate is so little soluble in water, that it is precipitated by the addition of carbonate of either sodium or potassium to a solution of a lithium compound. The phosphates of all the other members are readily soluble in water, while lithium phosphate is almost insoluble, and is precipitated from solutions of a lithium salt by the phosphates of either sodium or potassium. In these two compounds, the carbonate and phosphate, lithium behaves more like one of the metals of the alkaline earths.

All the metals of this family are monovalent, and replace each other, atom for atom, in chemical compounds.

POTASSIUM.

Symbol, K. Atomic weight = 39.15.

Occurrence.—In combination this element is widely distributed in nature. It forms an essential constituent of many of the common silicates and rocks which form the earth's crust. From these rocks, by processes of disintegration, the potassium com-

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* The student should consult special works on spectrum analysis.

pounds find their way into the soil, from whence they are absorbed by plants, which can only flourish in a soil that contains compounds of potassium. Most of the potassium found in plants is present in combination with organic acids.

From the vegetable kingdom, potash passes directly into the bodies of animals. The material known as *suint*, which is the oily perspiration of the sheep, that accumulates in, and is extracted from the wool, consists of the potassium salt of an organic acid (sudoric acid). In the form of chloride and sulphate, potassium is present in sea-water and many mineral springs. As nitrate it is found as a crystallised efflorescence upon the soil, notably in Peru and Chili, where it is associated with sodium nitrate. The largest

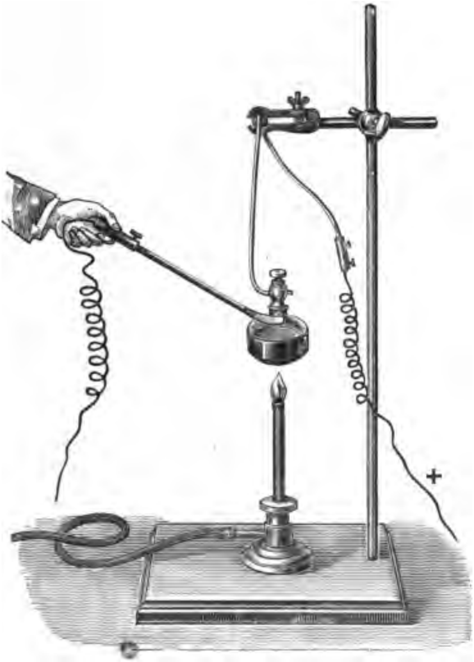

FIG. 131.

supplies of potassium compounds are met with in the great saline deposits of Stassfurt, where the element is found as chloride (KCl) in *sylvine*, as a double chloride of potassium and magnesium ($KCl,MgCl_2,6H_2O$) in *carnallite*, and as a mixed sulphate in *kainite* ($K_2SO_4,MgSO_4,MgCl_2,6H_2O$).

Modes of Formation.—(1.) The method by which Davy first effected the isolation of potassium was by the electrolysis of potassium hydroxide: the method may be illustrated by the experiment represented in Fig. 131. A small quantity of potassium hydroxide is gently heated in a platinum capsule, which is connected to the positive terminal of a powerful battery. A stout platinum wire, flattened out at one end, is made the cathode. When this is introduced into the fused potash, a brisk evolution of gas takes place, and minute beads of metallic potassium make their appearance in the liquid and upon the negative electrode, some of which ignite upon the surface. The decomposition takes place according to the equation—

$$2KHO = H_2 + O_2 + 2K.$$

(2.) Potassium may also be obtained by allowing melted potassium hydroxide to pass over iron turnings heated to whiteness, when the magnetic oxide of iron is formed—

$$4KHO + 3Fe = Fe_3O_4 + 2H_2 + 4K.$$

This is known as Gay-Lussac and Thénard's method.

(3.) The method devised by Brunner, and modified by Wöhler, Deville, and others, consisted in heating to whiteness an intimate mixture of potassium carbonate and carbon. This mixture was obtained by first igniting in a covered iron pot crude tartar (hydrogen potassium tartrate, or cream of tartar), which was thereby decomposed as indicated by the equation—

$$2HKC_4H_4O_6 = K_2CO_3 + 3C + 5H_2O + 4CO.$$

The charred mass was then introduced into an iron retort, and strongly heated in a furnace, when the potassium carbonate was reduced by the carbon, as follows—

$$K_2CO_3 + 2C = 3CO + 2K.$$

In this process there was frequently formed variable quantities of a highly explosive compound, owing to the union of potassium with carbon monoxide, believed to have the composition $K_6(CO)_6$.

(4.) Castner's process for the manufacture of potassium (1886) consisted in strongly heating potassium hydroxide with a carbide of iron, having approximately the composition CFe_2.

The potassium hydroxide, with the powdered carbide of iron, was introduced into large egg-shaped retorts, one of which is represented in Fig. 132. These retorts were placed upon hydraulic lifts, so that they could be lowered away from their covers, to the ground-level, in order to be discharged at the end of the distillation. The retorts were heated by gaseous fuel, and the metal, as it distilled, was passed into long narrow cast-iron condensers, from which it dropped into iron pots, and was protected from oxidation by mineral oil. The reaction which takes place may be represented by the equation—

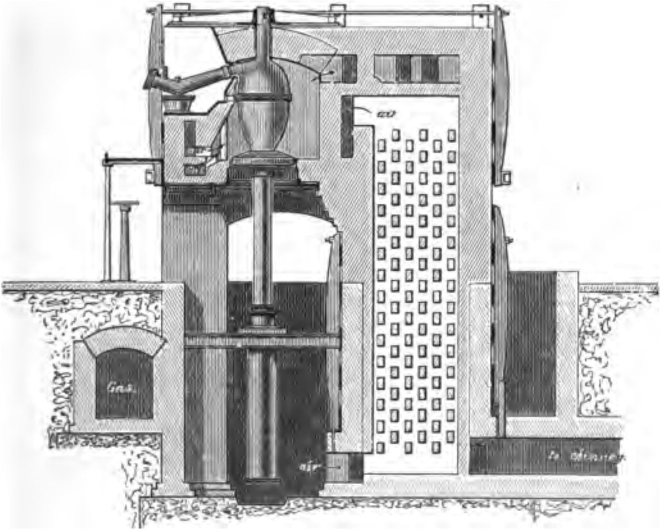

FIG. 132.

$$6KHO + 2C = 2K_2CO_3 + 3H_2 + 2K.$$

(5.) At the present time potassium is obtained almost exclusively by a modernised form of Davy's original method, namely, by the electrolysis of fused potassium hydroxide. The process is conducted precisely as described for the manufacture of sodium.

Properties.—Potassium is a lustrous white metal, which at ordinary temperatures is sufficiently soft to be moulded between the fingers; at 0° it is brittle, and shows a crystalline fracture. The metal is readily crystallised by melting a quantity of it in a vacuous tube, and when it has partially solidified, pouring the still liquid portion to the other end of the tube. Potassium melts at 62.5°, and when boiled gives an emerald-green vapour. The metal is rapidly acted on by ordinary air, its freshly cut surface becoming instantly covered with a film of oxide, which, by absorption of atmospheric moisture and carbon dioxide, passes first into the hydroxide and finally into the carbonate. Potassium is therefore usually preserved beneath naphtha, or some other liquid devoid of oxygen.

When potassium is volatilised in a vacuous tube, the thin film of metal which condenses upon the cool portion of the tube is seen to possess a rich violet-blue colour, when viewed by transmitted light. The density of potassium vapour is about 20 (Dewar and Scott), showing that in the vaporous condition the molecules are monatomic.

Potassium dissolves in liquefied ammonia, forming a deep indigo solution (page 276). When potassium is thrown upon water, that liquid is decomposed with sufficient energy to cause the ignition of the liberated hydrogen (page 172). When heated in carbon dioxide, potassium takes fire, forming potassium carbonate and carbon (page 304). Heated in carbon monoxide, it forms the explosive compound already mentioned. Potassium takes fire spontaneously in contact with the halogens, forming the haloid compounds of the metal. When heated in hydrogen, it absorbs the gas, forming a brittle lustrous substance, which inflames spontaneously in the air. This compound has the composition K_4H_2.

When heated in nitric oxide, potassium burns, forming a mixture of potassium nitrate and nitrite (Holt and Sims).

Oxides of Potassium.—When potassium is heated in ordinary air, it takes fire and burns, giving rise to a mixture of the oxides of the metal. *Perfectly dry* air or oxygen is without action upon potassium.

Potassium Peroxide, K_2O_4, may be obtained by melting potassium in an atmosphere of nitrogen, and gradually displacing the nitrogen by moderately dry oxygen. It is also produced by heating potassium in nitrous oxide.

Potassium peroxide is a yellow powder, which, when strongly heated, is converted into the dioxide K_2O_2 and oxygen. When thrown into water oxygen is evolved, potassium hydroxide and hydrogen peroxide being formed—

$$K_2O_4 + 2H_2O = 2KHO + H_2O_2 + O_2.$$

By the regulated combustion of potassium in nitrous oxide, Holt and Sims have obtained compounds having the composition K_2O_2 and K_2O_3. The latter, in contact with the air, undergoes active oxidation into K_2O_4.

Potassium Hydroxide (*caustic potash*), KHO, is prepared by adding lime to a dilute boiling solution of potassium carbonate, in iron vessels, when calcium carbonate is precipitated and potassium hydroxide remains in solution—

$$K_2CO_3 + Ca(HO)_2 = CaCO_3 + 2KHO,$$

the reaction being complete when the addition of an acid to a small test sample of the clear liquor produces no effervescence. This reaction is a reversible one, and if the concentration is beyond a certain limit, the potassium hydroxide reacts upon the calcium carbonate, reforming potassium carbonate. The liquid is therefore constantly maintained at a certain state of dilution during the reaction, at the completion of which the mixture is allowed to settle, and the clear solution is then partially concentrated in iron vessels, and finally in silver, until on cooling the substance solidifies. It is then usually cast into sticks.

Caustic potash is a white brittle solid ; it is extremely deliquescent, and dissolves in water with evolution of heat, forming a highly caustic liquid. The solid, as well as the solution, readily absorbs carbon dioxide, and is employed in the laboratory for this purpose when it is desired to deprive a gas of the last traces of any admixed carbon dioxide. A hot saturated solution of potassium hydroxide, when cooled, deposits crystals of a hydrate having the composition $KHO,2H_2O$.

Potassium Fluoride, KF.—This salt is prepared by neutralising aqueous hydrofluoric acid with potassium carbonate, and evaporating the solution in a platinum vessel, when the salt is obtained in the form of deliquescent cubical crystals. Potassium fluoride dissolves in aqueous hydrofluoric acid with evolution of heat, forming the acid fluoride of potassium, HF,KF, which is obtained as an anhydrous salt when the solution is evaporated to dryness and heated to 110°. This salt is not deliquescent. When heated to a dull red heat it decomposes into the normal salt and hydrofluoric acid (see p. 350).

Potassium Chloride, KCl.—This salt is found in sea-water, and was at one time obtained as a secondary product in the manufacture of bromine from sea salt, and of iodine from seaweed, as well as in various other industrial processes. At the present day it is almost exclusively obtained from the enormous deposits of carnallite at Stassfurt. The method by which potassium chloride is obtained from this double salt, $KCl,MgCl_2,6H_2O$, is based upon the fact, that when dissolved in water the salt dissociates into its two constituents; and when the solution is concentrated, the more insoluble potassium chloride first separates out, leaving the magnesium chloride in solution.

In practice, the crushed crude carnallite is treated with boiling mother-liquors from previous operations, in large tanks into which steam can be driven. These mother-liquors are practically a strong solution of magnesium chloride, and it is found that while potassium chloride is readily soluble in this liquid, the sodium chloride and magnesium sulphate which are present in the crude carnallite are only slightly dissolved by it, and are therefore left behind in the residue.

The muddy liquid is allowed to settle for about an hour, when it is drawn off into large iron crystallising tanks. The salt which is then deposited contains from 80 to 90 per cent. of potassium chloride, the remainder being mainly sodium and magnesium chlorides.

The mother-liquor from these crystallising tanks is either used again for treating a fresh charge of mineral, or is further evaporated, when crystals of *carnallite* separate out; for it is found that when the amount of magnesium chloride present is greater than three times the proportion of potassium chloride in the solution, the liquid on crystallising deposits the double chloride of the two metals. The impure potassium chloride from the crystallising tanks is purified by washing with cold water, in which the salt is only slightly soluble, and by subsequent recrystallisation. Potassium chloride crystallises, like the chlorides of sodium, rubidium, and caesium, in cubes.

Potassium Chlorate, $KClO_3$.—When chlorine is passed into a solution of potassium hydroxide, a mixture of potassium chlorate and chloride is obtained, thus—

$$6KHO+3Cl_2=KClO_3+5KCl+3H_2O.$$

The two salts in solution may be separated by crystallisation, the chlorate being much less soluble in cold water than the chloride.

On the manufacturing scale, potassium chlorate is obtained by passing chlorine into milk of lime, when a mixture of calcium chlorate and chloride is formed—

$$6Ca(HO)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

The operation is conducted in cast-iron cylinders connected in series, one of which is shown in section in Fig. 133, furnished with mechanical stirring gear, *a*, *b*, *b*. The shaft and the pipes conveying the chlorine into and from the vessel are connected to it by means of the water-sealed joints, *c*, *e*, *e*. The manhole *f* is a short wide leaden pipe, dipping a few inches into the liquid, which allows of the periodic withdrawal of samples for examination. Several reactions are involved in the final formation of the calcium chlorate; in the first case calcium hypochlorite is produced, thus—

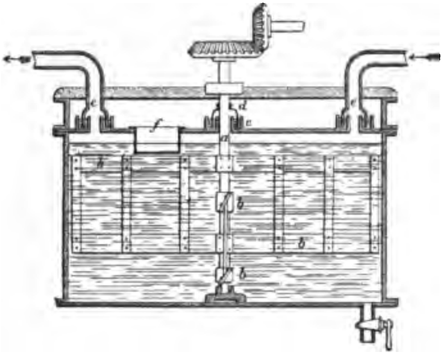

FIG. 133.

$$2Ca(HO)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

The calcium hypochlorite then passes into a mixture of chlorate and chloride in accordance with the equation—

$$3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2.$$

The second change is brought about by the operation of two causes, namely, rise of temperature and the presence of excess of chlorine. Heat *alone* is incapable of converting more than a small proportion of the hypochlorite into chlorate, for the former compound is at the same time decomposed into calcium chloride and free oxygen. The excess of chlorine is believed to act, through the intervention of hypochlorous acid, HOCl, merely as a carrier of oxygen, reducing two molecules of calcium hypochlorite to chloride, and oxidising the third to chlorate, thus—

$$3Ca(OCl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4HOCl + 2Ca(OCl)_2 = 2CaCl_2 + Ca(ClO_3)_2 + 2Cl_2 + 2H_2O.$$

The absorption of chlorine by the milk of lime is attended with evolution of heat; care is taken to prevent the temperature from rising above about 70°, otherwise loss results by the decomposition of hypochlorite with evolution of oxygen, thus—

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

When the formation of calcium chlorate is complete, the liquid is allowed to settle, and is then run into concentrating pans, where the requisite amount of potassium chloride in solution demanded by the following equation is added—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

The liquid is then concentrated in iron pans and allowed to crystallise, when the moderately soluble potassium chlorate separates out, leaving the very soluble calcium chloride in solution. The chlorate is afterwards purified by recrystallisation.

Potassium chlorate, although only moderately soluble in water, is much more soluble in a strong solution of calcium chloride, hence there is always a loss (usually about 10 per cent.) of chlorate in this process. Péchiney's process for obviating this consists in concentrating the liquid obtained by the chlorination of the lime to a definite specific gravity, and then cooling it to 12°, when about 78 per cent. of the calcium chloride crystallises out. The mother-liquor, containing all the calcium chlorate and only the comparatively small proportion of calcium chloride, is then treated with potassium chloride as usual.

Like so many of the older manufacturing processes, this for the preparation of potassium chlorate is now being displaced by modern electrolytic methods. A solution of potassium chloride is electrolysed in an undivided cell; the anode consisting of a thin sheet of platinum, and the cathode being a vertical grid of copper wire. The solution is caused to flow continuously through the electrolytic cell, the rate of flow being so regulated that the temperature of the liquid is maintained at about 50° C., and that the proportion of chlorate produced does not rise above 3 per cent. in the liquid. The dilute liquor is passed into suitable refrigerators, where the sparingly soluble chlorate crystallises out. The chemical action may be regarded as taking place in stages; the chlorine liberated at the anode there unites with oxygen and water, yielding hypochlorous acid—

$$2Cl + O + H_2O = 2HClO.$$

At the same time potassium hydroxide is produced at the cathode, with elimination of hydrogen. The caustic potash coming in contact with hypochlorous acid, or with chlorine, gives rise to potassium hypochlorite, which reacting with hypochlorous acid produces potassium chlorate—

$$KClO + 2HClO = KClO_3 + 2HCl.$$

Potassium chlorate crystallises in white tables, belonging to the monosymmetric system, which when of large size often exhibit fine iridescent colours. 100 parts of water at 0° dissolve 3.3 parts of the salt; while at 100°, 59 parts are dissolved.

Potassium chlorate is used largely in the manufacture of matches, on account of the ease with which it gives up its oxygen: thus, if a small quantity of the finely powdered salt be carefully mixed with an equally small amount of red phosphorus, the friction caused by lightly rubbing it with a spatula is sufficient to cause the mixture to detonate violently. Similarly, when powdered potassium chlorate and sulphur are rubbed together in a mortar, the mixture explodes with violence. Potassium chlorate is also largely employed in pyrotechny, especially in the production of coloured effects, where a fiercely burning mixture is required.

Potassium chlorate melts between 360° and 370°, and at a temperature about 380° begins to evolve oxygen.

Potassium Perchlorate, $KClO_4$.—When the chlorate is heated, it first melts and begins to give off oxygen; but it soon begins to partially solidify, owing to the formation of potassium perchlorate, and the evolution of oxygen stops unless a stronger heat be applied. The reaction at this stage may be expressed by the equation—

$$8KClO_3 = 5KClO_4 + 3KCl + 2O_2.$$

The evolution of oxygen, however, is not an *essential* condition of the formation of the perchlorate. By careful regulation of the temperature the following decomposition can be made to take place—

$$4KClO_3 = KCl + 3KClO_4.$$

The perchlorate is separated by first treating the residue with cold water, which dissolves the greater part of the chloride, and afterwards with warm hydrochloric acid, which decomposes any remaining chlorate. The salt is then purified by crystallisation.

Potassium perchlorate is very slightly soluble in cold water, 100 parts of water at 0° dissolving only 0.7 part of the salt; while at 100°, 20 parts are dissolved.

Potassium Bromide, KBr, and **Iodide,** KI.—These two salts are obtained by similar methods. When bromine or iodine is added to a solution of potassium hydroxide, the reaction which takes place is exactly analogous to that in the case of chlorine (see Potassium Chlorate, above)—

$$6KHO + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

If the solution so obtained be evaporated to dryness, and the dry residue ignited, the bromate (or iodate) is decomposed, just as potassium chlorate is decomposed by heat, giving off its oxygen, and being converted into bromide (or iodide)—

$$KBrO_3 = KBr + 3O.$$

The residue, on being dissolved in water and recrystallised, yields pure potassium bromide (or iodide).

These salts are manufactured by decomposing ferrous bromide, Fe_3Br_8 (or iodide, Fe_3I_8), with potassium carbonate, thus—

$$Fe_3Br_8 + 4K_2CO_3 = Fe_3O_4 + 8KBr + 4CO_2.$$

The ferrous bromide is obtained by adding bromine to moistened iron borings (see Manufacture of Bromine).

Potassium iodide and bromine both crystallise in cubes, and are both readily soluble in water. These salts are chiefly used for medicinal and photographic purposes.

Potassium Sulphate, K_2SO_4.—This salt is present in the Stassfurt deposits principally as *kainite*, $K_2SO_4, MgSO_4, MgCl_2, 6H_2O$, and as *polyhalite*, $K_2SO_4, MgSO_4, 2CaSO_4, 2H_2O$. When kainite is treated with small quantities of water, or mother-liquors from other processes, the extremely soluble magnesium chloride is removed, leaving the potassium magnesium sulphate; and on adding to this the requisite amount of potassium chloride, the following change takes place—

$$K_2SO_4,MgSO_4+3KCl=2K_2SO_4+KCl,MgCl_2.$$

From this solution the potassium sulphate crystallises out.

Potassium sulphate is also obtained by the action of sulphuric acid upon the chloride, by a process corresponding exactly to the first stage in the Leblanc soda process (*q.v.*)—

$$2KCl+H_2SO_4=K_2SO_4+2HCl.$$

Potassium sulphate forms colourless rhombic crystals, containing no water of crystallisation, therein differing from sodium sulphate, which crystallises with ten molecules of water.

Potassium sulphate is largely used for agricultural purposes.

Potassium Carbonate, K_2CO_3.—This salt was formerly obtained exclusively from the ashes of wood and other land plants, and was known under the name of *pot-ashes.* The process is still carried on in parts of Canada and the United States. The wood is burned in pits, and the ashes are collected and lixiviated with water (with the addition of a small quantity of lime) in wooden tubs with perforated false bottoms. The liquid which is drawn off is evaporated to dryness, and usually calcined to burn away the organic matter. This material, known as American pot-ashes, contains varying quantities of caustic potash, on account of the previously added lime. The so-called American *pearl-ash* is a purer product, obtained by concentrating the liquor from the lixiviating tubs until the less soluble impurities crystallise out, and finally evaporating the mother-liquor, containing the potassium carbonate, to dryness, and calcining the residue.

Potassium carbonate is also obtained from beet-root molasses, an uncrystallisable residue obtained in the manufacture of beet sugar, carried on chiefly in France. The syrup is fermented with yeast, whereby the sugar it contains is converted into alcohol, and then distilled. The residual liquid, known as *vinasse*, is evaporated to dryness; and from the black residue, termed "vinasse cinder," the potassium carbonate is extracted.

Potassium carbonate is obtained also from *suint*, which, as already stated, contains considerable quantities of potassium in the form of potassium sudorate. The sheep's wool is lixiviated with water, and the solution evaporated to dryness. The residue is heated in iron retorts, whereby the organic potassium salts are converted into carbonate, while, at the same time, ammonia and an illuminating gas are evolved. The carbonaceous residue is extracted with water, and the potassium carbonate separated by crystallisation.

Since the development of the Stassfurt potash supplies, these sources of potassium carbonate are rapidly sinking into the background, and the bulk of this compound is now manufactured from potassium sulphate by a process similar to the Leblanc soda process (*q.v.*).

Potassium carbonate is not manufactured by a method analogous to the ammonia-soda process (Solvay), on account of the too great solubility of potassium bicarbonate (hydrogen potassium carbonate).

Pure potassium carbonate may be obtained by igniting cream of tartar (see page 512), and extracting with water; or by heating hydrogen potassium carbonate, which gives up water and carbon dioxide, thus—

$$2HKCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium carbonate forms long prismatic crystals belonging to the monosymmetric system, and containing three molecules of water, $K_2CO_3,3H_2O$. The anhydrous salt is highly deliquescent, and very soluble in water.

Hydrogen Potassium Carbonate (*bicarbonate of potash*), $HKCO_3$, is produced by passing carbon dioxide into an aqueous solution of the normal carbonate, thus—

$$K_2CO_3 + CO_2 + H_2O = 2HKCO_3.$$

This salt is much less soluble in water than the normal salt, and is readily purified by crystallisation.

Potassium Nitrate (*nitre*, *saltpetre*), KNO_3.—This salt has been known since very early times. It occurs as an efflorescence upon the earth, as a result of the oxidation of organic nitrogenous matter in the presence of the potash in the soil, and is found in the neighbourhood of villages, more especially in hot climates, where urine and other readily decomposable organic matters rich in nitrogen find their way into the surface soil. It has been shown that the process of nitrification which results in the formation of nitre under these circumstances is due to the action of specific organisms, or microbes, and never takes place in their absence.

At various times this natural process has been artificially carried on, by mixing manure and other decomposing refuse with porous soil, lime, and wood ashes, and exposing the mixture in heaps which were moistened from time to time with drainage from manure. The *saltpetre earth*, collected from the natural sources or from the artificial *nitre plantations*, on lixiviation with water, and subsequent evaporation, yielded crystals of potassium nitrate.

At the present time potassium nitrate is almost exclusively obtained from sodium nitrate (*Chili saltpetre*), by treatment with potassium chloride derived from the Stassfurt supplies. The requisite quantities of the two solutions are run into a tank, and heated by means of steam, when the following double decomposition takes place—

$$NaNO_3 + KCl = NaCl + KNO_3.$$

The greater part of the sodium chloride is at once precipitated, and is removed by canvas filters. The clear liquid is then allowed to crystallise in tanks furnished with stirring gear, in order to cause the formation of small crystals, and the *nitre-meal* so obtained is purified by recrystallisation.

Potassium nitrate crystallises usually in rhombic prisms, but it can also be obtained in the form of small rhombohedral crystals, isomorphous with sodium nitrate.

The solubility of potassium nitrate rapidly increases with rise of temperature (see Solubility Curve, p. 152). 100 parts of water at 0° dissolve 13.3 parts; at 50°, 86 parts; and at 100°, 247 parts.

Nitre melts at 339°, and at a higher temperature loses oxygen and is converted into potassium nitrite; on this account it readily oxidises many of the elements when heated in contact with them. Thus, a fragment of charcoal or sulphur thrown upon melted nitre takes fire and burns with great energy; in the one case with formation of potassium carbonate and carbon dioxide, and in the other of potassium sulphate and sulphur dioxide—

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$
$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Nitre is chiefly used in the manufacture of gunpowder and in pyrotechny.

Gunpowder is a mixture of nitre, charcoal, and sulphur. The proportions in which these ingredients are present varies, within small limits, according to the special kind of powder, as will be seen from the following table (Abel and Nobel), giving analyses of various powders manufactured at Waltham Abbey.

	Fine-Grain.	Rifle Fine-Grain.	Rifle Large-Grain.	Pebble Powder.
Potassium nitrate	73.55	75.04	74.95	74.67
,, sulphate	0.36	0.14	0.15	0.09
Sulphur	10.02	9.93	10.27	10.07
Charcoal	14.59	14.09	13.52	14.22
Water	1.48	0.80	1.11	0.95

These proportions are very close to those which would be demanded by the equation—

$$2KNO_3+S+3C=K_2S+3CO_2+N_2,$$

which was at one time supposed to represent the change which takes place when gunpowder is exploded. In reality the decomposition is much more complex, and it has been shown that the solid products consist of mixtures of the following substances in varying proportions, depending upon the particular powder, and the conditions of firing—

Potassium carbonate.
,, sulphate.
,, sulphide.
,, thiosulphate.
,, thiocyanate.
Potassium nitrate.
,, oxide.
Ammonium sesquicarbonate.
Carbon.
Sulphur.

While the gases that are evolved consist of—

Carbon dioxide.
Nitrogen.
Carbon monoxide.
Sulphuretted hydrogen.
Marsh gas.
Oxygen.
Hydrogen.

From the combustion of one gramme of powder the total weight of solids ranges from 0.55 to 0.58 gramme, and the total weight of the gaseous products from 0.45 to 0.42 gramme.

Potassium Cyanide, KCN.—This salt is manufactured from potassium ferrocyanide, which is first obtained by heating in an iron pot a mixture of scrap iron, crude potashes, and waste animal refuse, such as hoofs, horns, hide, &c. The complex changes which take place do not at once result in the formation of the ferrocyanide, as this salt is unstable at high temperatures, but in the production of various compounds (the very stable salt potassium cyanide amongst them) which, when the mass is subsequently treated with water, interact, with the formation of potassium ferrocyanide. The aqueous extract is allowed to crystallise, and the ferrocyanide is obtained as large lemon-yellow prisms, with three molecules of water. When this compound is dried and heated alone it decomposes into potassium cyanide, free nitrogen, and a carbide of iron—

$$K_4Fe(CN)_6 = 4KCN + N_2 + FeC_2.$$

By heating the ferrocyanide with potassium carbonate a larger yield of the cyanide is obtained, mixed with potassium cyanate—

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2.$$

For many commercial uses for which potassium cyanide is required the presence of this cyanate is not detrimental.

If potassium ferrocyanide be heated with metallic sodium the whole of the cyanogen it contains is converted into alkali cyanide (Erlenmeyer)—

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The mixed potassium and sodium cyanide thus obtained is well suited for the technical processes for which cyanide is required.

Potassium cyanide is a white solid which is extremely soluble in water, from which it crystallises in white anhydrous plates. When heated the salt readily fuses, but is stable at very high temperatures, being capable of being volatilised without decomposition. In the fused state it is a powerful reducing agent, taking up oxygen to yield potassium cyanate, KCNO.

COMPOUNDS OF POTASSIUM WITH SULPHUR.

Four sulphides of potassium have been obtained, namely—

Potassium monosulphide	K_2S
Potassium trisulphide	K_2S_3
Potassium tetrasulphide	K_2S_4
Potassium pentasulphide	K_2S_5

Just as potassium decomposes water with evolution of hydrogen and formation of potassium hydroxide, so also, when heated in sulphuretted hydrogen (the sulphur analogue of water) it forms potassium hydrosulphide (the analogue of potassium hydroxide) and liberates hydrogen, thus—

$$H_2S + K = KHS + H.$$

When potassium hydroxide and hydrosulphide are mixed in equimolecular proportions, potassium monosulphide and water are formed—

$$KHO + KHS = K_2S + H_2O.$$

The liquid, on evaporation in vacuo, deposits reddish prismatic deliquescent crystals having the composition $K_2S,5H_2O$.

When potassium carbonate and sulphur are heated together a mixture of the higher sulphides of potassium with potassium thiosulphate is obtained, thus—

$$3K_2CO_3 + 8S = 2K_2S_3 + K_2S_2O_3 + 3CO_2.$$
$$3K_2CO_3 + 12S = 2K_2S_5 + K_2S_2O_3 + 3CO_2.$$

The reddish-brown solid product was named by the early chemists *hepar sulphuris*, or "liver of sulphur."

SODIUM.

Symbol, Na = 23.05.

Occurrence.—The most abundant natural compound of sodium is the chloride, which is present in sea-water and in many salt lakes and springs. Enormous deposits of sodium chloride or *rock-salt* are found in Cheshire, Lancashire, and other parts of the world. As nitrate, this element occurs in large quantities in Chili and Peru, and in combination with silicic acid it is a constituent of many rocks.

Modes of Formation.—Sodium was first isolated by Davy, by the electrolysis of sodium hydroxide. On a manufacturing scale it has been obtained by the various processes described under potassium, the history of the commercial preparation of these two elements being practically identical. Sodium, however, does not form any explosive compound with carbon monoxide, so that the manufacture in this case has been free from this difficulty.

At the present time sodium (and also potassium) is almost exclusively obtained by electrolytic methods.

(1.) *Castner's Process.*—This method consists in the electrolysis of fused sodium hydroxide, and is, in fact, simply the original process by which Davy first obtained the metal adapted to modern resources of electrical power. The apparatus employed is shown in section in Fig. 134. The caustic soda is contained in an iron pot P, set in suitable brick-work, and is kept in a melted state by a ring of gas flames below. Through the bottom of this vessel passes the cathode, which is maintained steady in its position by the caustic soda in the lower and narrow part of vessel P being in the solidified state. The anodes A are suspended from above round the cathode, and are prevented from touching it by means of a wirework cylinder which hangs from the vessel V. This vessel is an iron cylinder having a lid at the top, and is the receiver in which the sodium collects.

The products of the electrolysis are oxygen, hydrogen, and sodium. The oxygen liberated at the anodes escapes by the opening O in the lid. The sodium floats up to the surface of the molten caustic in the receiver V, and is withdrawn from time to time by means of a perforated ladle, which allows the caustic to drain through, but holds the liquid metal, owing to the extremely high surface tension of the latter. The hydrogen which is also liberated at the cathode escapes through the loosely fitting lid of the receiver.*

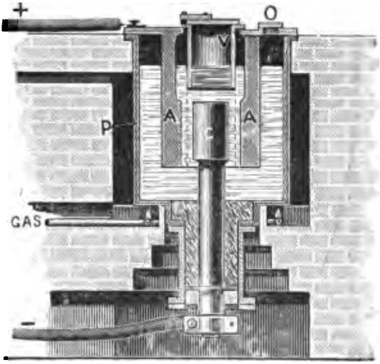

FIG. 134.

(2.) *Borchers' Process.*—It will be evident from an economic (and therefore the manufacturer's) point of view that the hydrogen liberated in the above process represents wasted electrical energy. Many attempts, therefore, have been made to substitute fused sodium chloride for the hydroxide. The practical difficulties to be overcome in this case are more serious, owing partly to the higher temperature required, and also to the corrosive action exerted by the fused chloride upon the materials of which the vessels are constructed. On the other hand, it will be evident that *both* the products of the electrolysis in this case will have commercial value. Borchers' apparatus is shown in section in Fig. 135. It

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* This process is extensively employed at Oldbury, near Birmingham, and at the works of the Niagara Electrical Company.

consists essentially of a U-tube made in two parts, the wide limb being of fireclay and the narrow part of iron, the two parts being clamped together. To prevent leakage at the joint, a square tube W is interposed between the two parts, which is kept cool by a flow of water through it. This causes the solidification of the sodium chloride in the form of a layer all round the junction. Chlorine is liberated at the anode and escapes by the pipe P. The narrow limb C is itself the cathode, and the sodium there produced overflows down the side pipe into a suitable receiver. Fresh sodium chloride is added as required through the tube D.

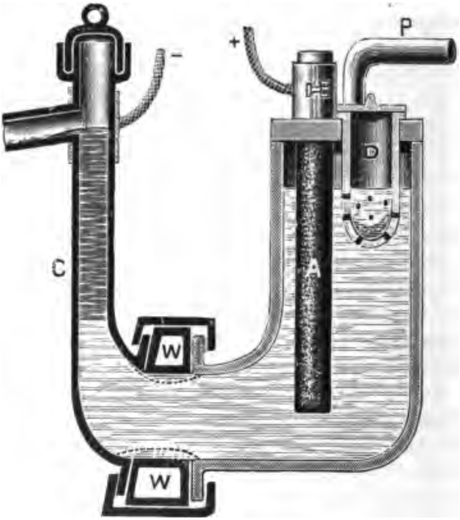

FIG. 135.

Properties.—Sodium closely resembles potassium in its general properties. It is a soft, white metal which can be readily moulded by the fingers, and is easily pressed into wire. At −20° it is hard. The colour of sodium vapour is violet, while the colour exhibited by a thin film of the metal, obtained by sublimation in vacuo, is greenish-blue. The vapour-density of sodium is about 12 (Dewar and Scott), showing that this metal in the vaporous state is monatomic.

Like potassium, sodium dissolves in liquid ammonia, yielding a blue solution. When heated in the air, sodium burns, forming the peroxide, Na_2O_2. Perfectly dry air or oxygen is without action upon the metal.

When heated in hydrogen, sodium forms the hydride, Na_4H_2, analogous to the potassium compound, but not spontaneously inflammable in air. When this is heated to about 300° in vacuo the whole of the hydrogen is evolved.

Alloy of Sodium and Potassium.—When these two metals are melted together beneath petroleum an alloy is obtained which is liquid at ordinary temperatures. When prepared and preserved out of contact with air the alloy resembles mercury in appearance. This alloy is employed in the construction of thermometers for registering high temperatures, where mercury would be inadmissible.

Oxides of Sodium.—Two oxides are said to exist, viz., sodium monoxide, Na_2O, and sodium dioxide, or peroxide, Na_2O_2.

Sodium Monoxide, Na_2O,* is said to be obtained by burning sodium in nitrous oxide at a temperature not higher than 180°.

Sodium Peroxide, Na_2O_2, is obtained by allowing sodium to burn briskly in oxygen. It is a yellowish-white solid, which decomposes in contact with water, with considerable rise of temperature and evolution of oxygen—

$$Na_2O_2 + H_2O = 2NaHO + O.$$

The oxygen which is evolved contains appreciable quantities of ozone. When sodium peroxide is slowly added to water or to dilute hydrochloric acid in the cold, hydrogen peroxide is formed—

$$Na_2O_2 + 2H_2O = 2NaHO + H_2O_2.$$

Owing to the readiness with which it gives up oxygen, sodium peroxide is a powerful oxidising agent, and as such finds many uses in the laboratory. Thus it readily converts chromic compounds into chromates.

Sodium peroxide forms a crystalline hydrate of the composition, $Na_2O_2,8H_2O$ (page 228). When heated in either nitrous or nitric

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* Considerable doubt has been thrown upon the existence of this oxide. Erdmann and Köthner (*Annalen der Chemie*, Nov. 1896) have shown that rubidium and potassium do not form oxides of the type R_2O. And although lithium, the first member of the series, undoubtedly yields the oxide Li_2O, it appears doubtful whether sodium is capable of forming a similar compound.

oxides it yields sodium nitrite; in the former case with the elimination of nitrogen—

$$Na_2O_2+2N_2O=2NaNO_2+N_2.$$
$$Na_2O_2+2NO=2NaNO_2.$$

Sodium Hydroxide (*caustic soda*), NaHO.—This compound is produced when sodium is brought into contact with water, and also when either sodium monoxide or peroxide is dissolved in water. On the large scale caustic soda is prepared by the action of lime upon a boiling solution of sodium carbonate (see Caustic Potash).

The so-called *tank liquors* (obtained in the manufacture of sodium carbonate by the Leblanc process, *q.v.*) are heated to the boiling-point, and an excess of lime is stirred into the mixture. The sodium sulphide present in the tank liquor is oxidised into sulphate by the combined action of air injected into the mixture, and of sodium nitrate, which is added for this purpose. The liquor, after being causticised, is decanted or filtered from the precipitated calcium carbonate, and is concentrated in large cast-iron hemispherical pans. The decomposition suffered by the sodium nitrate depends upon the temperature and concentration of the liquid; at 300° to 360° the change may be expressed by the equation—

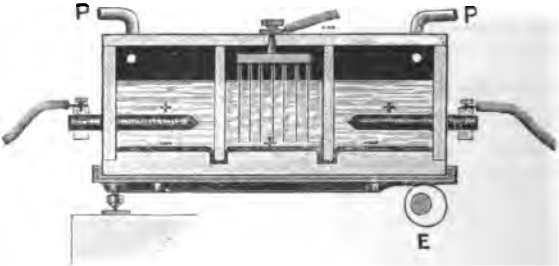

FIG. 136.

$$NaNO_3+2H_2O=NaHO+NH_3+4O.$$

The liberated oxygen oxidises the sulphides to sulphates.

Caustic soda is now being manufactured by the electrolysis of brine. The apparatus devised by Castner for this purpose is seen in Fig. 136. It consists of a rectangular vessel divided into three compartments. Upon the floor of the vessel there is a layer of mercury about ⅛th of an inch deep. The partitions, which are non-porous, dip into narrow gutters across the bottom, but do not actually touch the bottom, so that when the tank is gently oscillated the mercury can flow from one compartment to the other, while the liquid above is prevented from so doing. The two outside compartments are filled with brine, while the centre one contains water; and in this is placed the cathode, consisting of a number of metal plates. Since the partitions are non-porous the current will pass from the carbon anodes through the salt solution to the mercury, which in the two extreme compartments then becomes the cathode. It then passes from the mercury in the middle space, which now becomes the anode of this cell, through the aqueous liquid to the metal cathode which is there suspended. In the outside compartments the sodium chloride is electrolysed; the chlorine discharged at the carbon anodes escapes by the pipes P P, while the sodium dissolves in the mercury cathodes. During the process a slow rocking movement is given to the tank by means of the excentric represented at E, whereby the mercury is caused to flow to and fro along the bottom. In the middle compartment the sodium contained in the amalgam is transported to the cathode, where it dissolves in the water, forming sodium hydroxide.

Sodium hydroxide is a white, strongly caustic, and highly deliquescent solid. It is soluble in water, with considerable rise of temperature, and a concentrated aqueous solution when cooled to $-8°$, deposits a crystalline hydrate, having the composition $2NaHO,7H_2O$.

Sodium Chloride, $NaCl$.—Of the compounds of sodium with the halogens the chloride is the most important. In warm climates, as upon the shores of the Mediterranean, sodium chloride is obtained by the evaporation of sea-water in large shallow basins or pools, constructed upon the sea-shore and exposed to the sun's heat. As the brine concentrates in these *salterns*, the crystals of salt are raked off the liquid and allowed to drain in heaps at the side of the pools. The mother-liquors, known as *bittern*, were formerly utilised for the extraction of the bromine which they contain.

Salt is obtained from salt-beds, where it is found in enormous deposits, either by direct mining operations, when the salt is sufficiently pure, or by first dissolving the material in water, whereby insoluble admixed impurities are removed, and afterwards evaporating the brine so obtained. The latter method is carried out by sinking borings through the upper strata of rock, and sending water down to the salt-beds beneath. The brine is then pumped up and the salt obtained by evaporation. The first stage of the concentrating process, especially where the brine is not very strong, is in some parts carried on by exposing the liquid to the wind. This is effected by causing the solution to trickle over erections of brushwood known as *graduators* (Fig. 137), which are built so that the prevailing winds blow across them. The brine is pumped up into the wooden troughs running along the top, from which it escapes by a number of openings, *a*, *a*, *a*, and flows over the pile of brushwood down into the reservoir upon which the

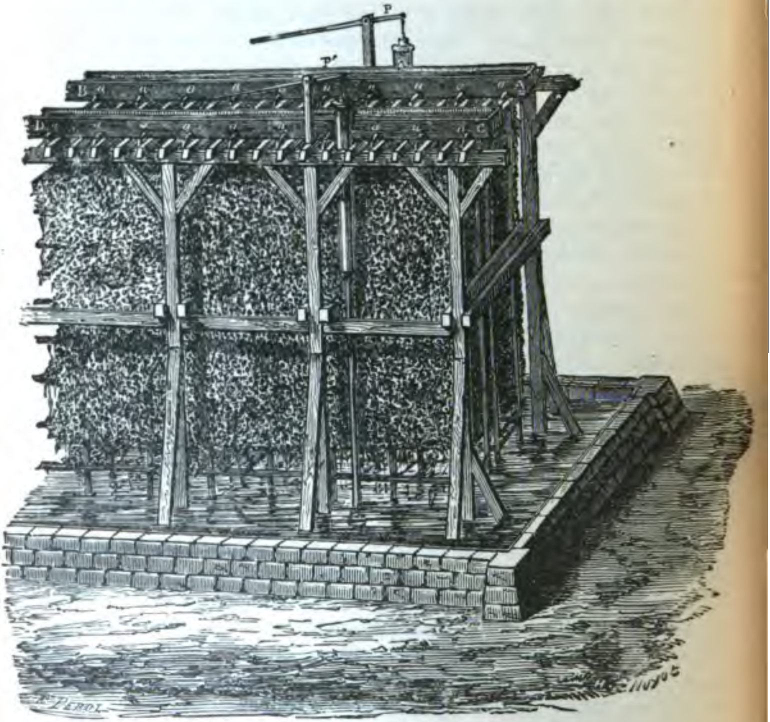

FIG. 137.

erection is constructed. In this way the solution is made to expose a large surface to the air, and it quickly reaches a concentration when it contains 20 per cent. of salt in the solution. The liquor is then evaporated in shallow iron pans by means of artificial heat, and as the salt crystallises it is lifted out by means of perforated iron skimmers. Salt obtained in this manner always contains small quantities of other salts, such as sodium sulphate, calcium sulphate, calcium and magnesium chlorides. The presence of chlorides of magnesium or calcium causes the salt to become moist, especially in damp weather.

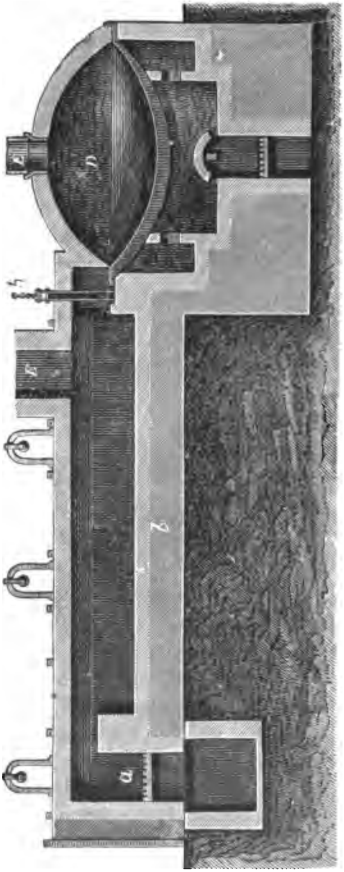

Fig. 138.

Pure sodium chloride may be prepared by adding hydrochloric acid to a strong aqueous solution of salt ; the sodium chloride is thereby precipitated, while the other salts remain in solution.

Sodium chloride forms colourless, cubical crystals, which are anhydrous. If deposited at – 10° it crystallises in monosymmetric prisms, with two molecules of water of crystallisation, which at the ordinary temperature lose their water and break up into minute cubes.

Sodium chloride is a necessary article of food for man and other animals ; it is estimated that about 20 lbs. of salt per head of population is annually used, directly or indirectly, for this purpose.

The hydrochloric acid present in the gastric and other acid fluids of the stomach is derived from the decomposition of sodium chloride which is taken into the organism.

Enormous quantities of sodium chloride are employed in the alkali industry, and all the chlorine that is manufactured is derived primarily from this compound.

Sodium Bromide, NaBr, and **Sodium Iodide,** NaI, are prepared by methods similar to those for obtaining the potassium compounds. They are both isomorphous with sodium chloride, and when deposited at low temperatures they form monosymmetric crystals containing two molecules of water.

Sodium Carbonate, Na_2CO_3.—The preparation of this compound is carried on by three methods, and constitutes that important industry, the *alkali manufacture.* Two of these processes are known by the names of their respective discoverers, namely, the *Leblanc* process and the *Solvay* process, the latter being also known as the *ammonia-soda* process. The third is a modern electrolytic method.

I. The Leblanc method of manufacture consists essentially of three processes, namely—

(1.) The conversion of sodium chloride into sodium sulphate by the action of sulphuric acid, known as the *salt-cake* process. Two chemical reactions are involved in the process—

$$\begin{aligned} NaCl + H_2SO_4 &= NaHSO_4 + HCl. \\ NaCl + NaHSO_4 &= Na_2SO_4 + HCl. \end{aligned}$$

(2.) The decomposition of sodium sulphate, *salt-cake,* by means of calcium carbonate (limestone) and coal, at a high temperature, whereby a crude mixture of sodium carbonate and calcium sulphide is obtained, known as *black-ash.* This black-ash process takes place in accordance with the following equation—

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2.$$

The change may be conveniently regarded as taking place in two stages, which proceed simultaneously according to the equations—

$$\begin{aligned} Na_2SO_4 + 2C &= Na_2S + 2CO_2. \\ Na_2S + CaCO_3 &= CaS + Na_2CO_3. \end{aligned}$$

(3.) The process of extracting and purifying the sodium carbonate contained in the *black-ash.*

(1.) *The Salt-cake Process.*—The first stage of this process is usually carried on in a large cast-iron pan (*D*, Fig. 138), built into a furnace in such a manner that it shall be heated as uniformly as possible. The charge of common salt is placed in the covered pan, and the requisite quantity of sulphuric acid is then run in. Hydrochloric acid is given off in torrents, according to the first of the above equations, and the gas is led away by the pipe *E* in the arched roof to the condensing-towers, where it is absorbed by water (see Hydrochloric Acid, page 369). The mixture is heated until it begins to stiffen into a solid mass, when the damper *h* is raised and the mass is raked out of the pan on to the hearth of the *roaster* or reverberatory furnace, *b*. Here it is exposed to the hot gases from the coke fire *a*, which sweep over it and ultimately raise its temperature nearly to a red heat, whereby the second of the above reactions is completed. The acid gas, together with the fire gases, leave the roaster by the chimney *e*, and are also led to condensing-towers, where the hydrochloric acid is absorbed. The mass is from time to time raked or worked by means of side-openings or "working doors" in the roaster, and as soon as the operation is completed the salt-cake is withdrawn. The salt-cake so obtained usually contains from 95 to 96 per cent. of normal

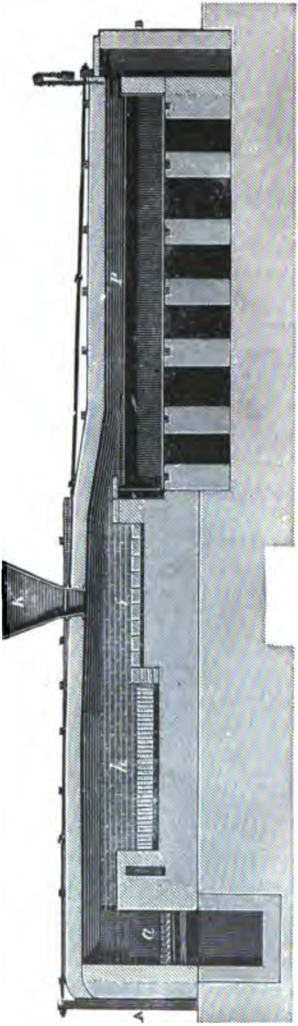

FIG. 139.

sodium sulphate, Na_2SO_4 ; the remaining 4 or 5 per cent. consisting of hydrogen sodium sulphate, $NaHSO_4$, undecomposed sodium chloride, and such impurities as were originally present in the salt.

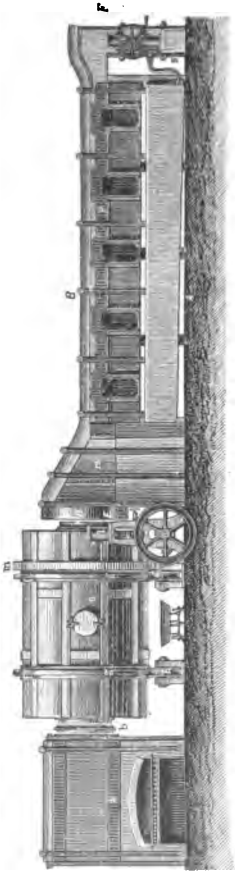

FIG. 140.

(2.) *The Black-ash Process.*—The salt-cake is mixed with limestone (or chalk) and coal dust (*slack*), and heated in a reverberatory furnace known as the black-ash or *balling* furnace. As the mixture softens with the heat it requires to be thoroughly mixed together, which, in the older forms of furnace (still used in many places), is accomplished by manual labour. Fig. 139 shows such a furnace in section. The materials are introduced by the hopper *k* on to the hearth *i*, where they are exposed to the hot gases from the fire *a* ; and as the decomposition proceeds they are raked along to the more strongly-heated front portion of the hearth *h*. During this process carbon dioxide is freely evolved, the escaping bubbles of gas giving the semi-fluid mass the appearance of boiling. As the temperature rises and the process approaches completion, the mass thickens, when it is worked up into large balls by means of rakes or *paddles*. At this stage carbon monoxide begins to be evolved, the bubbles of which, bursting from the doughy material, become ignited and burn upon its surface as small jets of flame coloured yellow by the soda. As soon as these appear the ball is quickly withdrawn from the furnace. The formation of carbon monoxide at the high temperature reached at this point in the process is due to the action of carbon upon the limestone according to the equation—

$$CaCO_3 + C = CaO + 2CO,$$

excess of these materials being intentionally present in the mixture. The effect of the escaping carbon monoxide at this point in the process, in rendering the black-ash light and porous (an important consideration in view of the next operation), is similar to that of baking-powder when used for cooking purposes. The heated gases from the furnace are made to pass over large evaporating pans, *P*, where liquors from a subsequent process are concentrated.

In the more modern forms of black-ash furnace, the mixing and working up of the materials is accomplished mechanically by means of a revolving hearth. Fig. 140 shows the general arrangement of a revolving black-ash furnace. The mixture is placed in the cylinder *e*, which is made to slowly revolve upon its horizontal axis. The heated gases from the fire *a* pass through this revolving hearth; they are then conveyed through a dust-chamber, *m*, and finally over concentrating-pans. Limestone and two-thirds of the coal are first thrown into the furnace and heated until the blue flame of burning carbon monoxide makes its appearance, when the salt-cake along with the rest of the coal is added, and the process continued until the yellow flames appear upon the surface of the mass. The contents of the cylinder are then thrown out into iron trucks beneath.

Black-ash is a mixture of variable composition, containing—

Sodium carbonate, Na_2CO_3 .	from	40	to	45	per cent.
Calcium sulphide, CaS . .	,,	30	,,	33	,,
Calcium carbonate, $CaCO_3$.	,,	6	,,	10	,,
Coke	,,	4	,,	7	,,
Calcium oxide, CaO . .	,,	2	,,	6	,,

And smaller quantities of sodium chloride, sodium sulphate, sodium sulphite, sodium sulphide, sodium thiosulphate, oxides of iron and alumina.

(3.) *Lixiviation of Black-ash.*—The lixiviation of black-ash is carried on in a series of tanks, so arranged that the liquid can be made to pass from one to the other. The action of water upon the black-ash is more than a simple process of dissolving the sodium carbonate from the mixture, for in the presence of water chemical action takes place between some of the ingredients. Thus the lime reacts upon sodium carbonate, forming sodium hydroxide, hence the *tank liquor* always contains caustic soda in varying quantities. Under certain conditions of temperature and dilution, the calcium sulphide also reacts upon the sodium carbonate, forming sodium sulphide and calcium carbonate, thus—

$$CaS + Na_2CO_3 = CaCO_3 + Na_2S.$$

Also by the oxidising influence of atmospheric oxygen, calcium sulphide, CaS, is converted into calcium sulphate, $CaSO_4$, which in its turn is acted upon by the sodium carbonate, involving loss of this product—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The process of lixiviation is carried on as rapidly as possible, and at temperatures ranging from about 30° (for the dilute liquors) to about 60° (for those more concentrated); for the formation of sodium sulphide diminishes as the concentration of the liquid increases. The tank liquor, after settling, is then either at once concentrated by evaporation, when the soda crystallises out, leaving the caustic soda in the mother-liquor, or it is submitted to the action of carbon dioxide, whereby both the caustic soda and the sodium sulphide are converted into sodium carbonate, thus—

$$2NaHO + CO_2 = Na_2CO_3 + H_2O.$$
$$Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S.$$

The concentration of the tank liquor is accomplished in the shallow pans above mentioned, by means of the waste heat from the black-ash furnace; and the product obtained by evaporating the liquid is usually calcined at a red heat in an ordinary reverberatory furnace. This substance is known as *soda-ash*, and when dissolved in water, and the solution allowed to crystallise, the so-called *soda crystals* are obtained, having the composition $Na_2CO_3,10H_2O$.

II. *The Ammonia-Soda Process.*—This process is based upon the fact, that hydrogen ammonium carbonate (*bicarbonate of ammonia*) is decomposed by a strong solution of sodium chloride, according to the equation—

$$H(NH_4)CO_3 + NaCl = HNaCO_3 + NH_4Cl.$$

In practice the brine is first saturated with ammonia gas, and the cooled ammoniacal liquid is then charged with carbon dioxide, under moderate pressure, in carbonating towers.

The hydrogen sodium carbonate (*bicarbonate of soda*), being much less soluble, separates out, leaving the more soluble ammonium chloride in solution, from which the ammonia is recovered by subsequent treatment with lime.

The hydrogen sodium carbonate is converted into normal sodium carbonate by calcination, and the carbon dioxide evolved is again utilised in carbonating a further quantity of ammoniacal brine—

$$2HNaCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

These two processes, namely, the *Leblanc* and the *ammonia-soda* process, have been keen competitors for a number of years; and a glance at the figures giving the annual output from the two sources shows how rapidly and steadily the younger process has gained upon its older rival. Indeed, there can be little doubt that but for the value of the hydrochloric acid which is simultaneously produced in the Leblanc process, this method would before now have ceased to exist as a manufacture. Now, however, both of these processes are threatened by the advent of a new and formidable rival in the electrolytic method.

III. *The Electrolytic Process* (Hargreaves-Bird).—In this method a solution of sodium chloride (brine, pumped direct from the salt-beds) is submitted to electrolysis in a cell of special construction. This consists of an oblong box divided longitudinally into three compartments, the centre one being comparatively large, while the two extreme compartments are quite narrow. The partitions which divide the box in this manner are made of a "composition" consisting largely of asbestos; and are of such a nature that when the middle compartment is filled with brine, none of the liquid percolates or oozes through into the side chambers. These asbestos diaphragms are backed on their outer sides by a network of copper wire which is made the cathode in the system. The anode consists of pieces of gas-carbon which are suspended in the brine in the centre chamber. Although the asbestos diaphragms are water-tight, in the sense that they do not allow the brine to pass from the middle to the outer compartments, they are nevertheless sufficiently porous to keep the copper wire cathodes moist, and to allow therefore of the passage of the current. Chlorine is evolved at the anode, and is conveyed away directly to lime chambers and converted into bleaching-powder. The sodium ions pass freely through the asbestos partitions to the cathodes, there generating sodium hydroxide; while a stream of steam and carbon dioxide which is passed through the narrow compartments immediately converts the hydroxide into carbonate, which is thus washed away from the cathodes as fast as it is formed. The solution so obtained is sufficiently concentrated to deposit crystals of sodium carbonate on cooling.

The "soda" obtained by this process, which is now being carried out on an extensive scale at Middlewich, Cheshire, is extremely pure, containing from 97 to 98 per cent. of sodium carbonate, and only about 1 per cent. of sodium chloride.

Sodium carbonate crystallises in large, transparent, monosymmetric crystals, commonly known as "soda" or "washing-soda," having the composition $Na_2CO_3,10H_2O$. On exposure to the air the crystals give up water, and become effloresced upon the surface, and finally fall to powder, having the composition Na_2CO_3,H_2O. When crystallised from hot solutions, it forms rhombic crystals, containing $7H_2O$. The solubility of sodium carbonate in water increases with rise of temperature, reaching a maximum at 32.5°, when 100 parts of water dissolve 59 parts of the salt. Above this temperature the solubility falls, and at 100° the amount dissolved is 45.4 parts.

Hydrogen Sodium Carbonate (*bicarbonate of soda*), $HNaCO_3$, may be obtained by the action of carbon dioxide upon the normal carbonate, either in solution or as crystals—

$$Na_2CO_3,10H_2O + CO_2 = 2HNaCO_3 + 9H_2O.$$

The greater part of the bicarbonate of soda of commerce is obtained in the ammonia-soda process above described.

This salt is less soluble in water than the normal carbonate. Thus, 100 parts of water at different temperatures dissolve the following quantities of these compounds—

	10°.	20°.	30°.	40°.
Na_2CO_3 . . .	12.6	21.4	38.1	50 parts.
$HNaCO_3$ . .	8.8	9.8	10.8	11.7 „

When a solution of hydrogen sodium carbonate is heated, the salt gives off a portion of its carbon dioxide, and on cooling the solution deposits crystals having the composition $Na_2CO_3,2HNaCO_3,2H_2O$, known as sodium sesquicarbonate. On continued boiling, the salt is completely converted into the normal carbonate. Sodium sesquicarbonate occurs as a natural deposit in Egypt, Africa, South America, and elsewhere, known as *trona*, from which the name *natrium* is derived.

Sodium Sulphate (*Glauber's salt*), $Na_2SO_4,10H_2O$, occurs native in the anhydrous condition as the mineral *thenardite*, and as a double sulphate of sodium and calcium, $Na_2SO_4,CaSO_4$, in the mineral *Glauberite.*

It is manufactured in immense quantities in the first (*salt-cake*) process in the alkali manufacture, by the Leblanc method.

It is also obtained in large supplies from the Stassfurt deposits, by double decomposition between magnesium sulphate (from *kieserite*) and sodium chloride.

The solution of the mixed salts, when cooled a few degrees below 0°, deposits sodium sulphate, and the soluble magnesium chloride remains in solution—

$$2NaCl + MgSO_4 = Na_2SO_4 + MgCl_2.$$

Sodium sulphate is also manufactured by the action of sulphur dioxide and oxygen upon sodium chloride. This is known as *Hargreave's process.* The reaction is expressed by the equation—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

This process is, in essence, the production of sodium sulphate from sodium chloride and the *constituents of sulphuric acid*, without the intermediate manufacture of the acid. The gases from pyrites burners, similar to those used by the "vitriol" manufacturer, together with steam, are passed through a series of cast-iron cylinders containing sodium chloride, and maintained at a temperature of 500° to 550°. Many days are required for the complete conversion of the chloride into sulphate by this process.

Sodium sulphate crystallises in colourless prisms belonging to the monosymmetric system, containing ten molecules of water; when exposed to the air the crystals effloresce, and when heated to 33° they melt in their own water of crystallisation (see page 153).

When sodium sulphate is heated with sulphuric acid, in the proportions required by the following equation, hydrogen sodium sulphate is formed—

$$Na_2SO_4 + H_2SO_4 = 2HNaSO_4.$$

Sodium Nitrate, $NaNO_3$, occurs associated with other salts in Bolivia and Peru, as *cubical nitre*, or *Chili saltpetre.* The crude salt is purified by solution in water, and crystallisation. It forms rhombohedral crystals, isomorphous with calcspar.

Sodium nitrate is very soluble in water. 100 parts of water dissolve at 0°, 68.8 parts; at 40°, 102 parts; and at 100°, 180 parts of the salt. When exposed to the air, the salt absorbs moisture, and on this account cannot be employed as a substitute for potassium nitrate in the manufacture of gunpowder, or in pyrotechny. Its chief uses are for the manufacture of nitric acid; for the manufacture of potassium nitrate by double decomposition with potassium chloride; and as an ingredient in artificial manures.

Sodium Phosphates.—The most important of these compounds is the hydrogen disodium orthophosphate, or common *phosphate of soda*, HNa_2PO_4. This salt is prepared on a large scale, by adding sodium carbonate to phosphoric acid until the solution is alkaline, and then filtering and evaporating the solution, when large transparent prisms, belonging to the monosymmetric system, are deposited, having the composition $HNa_2PO_4,12H_2O$. Exposed to the air the crystals effloresce, and when heated become anhydrous. The salt melts at 35°.

100 parts of water at 10° dissolve 4.1 parts; at 50°, 43.3 parts; and at 100°, 108.2 parts of the anhydrous salt.

Normal Sodium Orthophosphate, Na_3PO_4, is obtained from hydrogen disodium phosphate, by evaporating a solution of the latter salt with sodium hydroxide, until the liquid crystallises—

$$HNa_2PO_4 + NaHO = Na_3PO_4 + H_2O.$$

This salt contains twelve molecules of water, and forms thin six-sided prisms. Its aqueous solution is strongly alkaline, and absorbs atmospheric carbon dioxide, with the formation of hydrogen sodium carbonate and hydrogen disodium phosphate, thus—

$$Na_3PO_4 + CO_2 + H_2O = HNa_2PO_4 + HNaCO_3.$$

Dihydrogen Sodium Orthophosphate, H_2NaPO_4, is obtained when phosphoric acid is added to ordinary phosphate of soda, until the liquid gives no precipitate with barium chloride. On evaporating the solution, the salt crystallises—

$$HNa_2PO_4 + H_3PO_4 = 2H_2NaPO_4.$$

The aqueous solution of this salt is acid.

Hydrogen Sodium Ammonium Phosphate (*microcosmic salt*), $HNa(NH_4)PO_4,4H_2O$, is obtained by adding a strong solution of common sodium phosphate to ammonium chloride—

$$HNa_2PO_4+NH_4Cl=NaCl+HNa(NH_4)PO_4.$$

The orthophosphates are readily converted into pyro- and metaphosphates (see page 476).

LITHIUM.

Symbol, Li. Atomic weight=7.03.

Occurrence.—Lithium is only found in combination with other elements. It is a constituent of a few somewhat rare minerals, as *petalite*, $30SiO_2,4Al_2O_3,Na_2O,2Li_2O$; *spodumene*, $15SiO_2,4Al_2O_3,3Li_2O$; *lepidolite*, or *lithium mica*, $9SiO_2,3Al_2O_3,K_2O,4LiF$.

By means of the spectroscope, lithium compounds have been detected in sea-water, and in most spring and river waters. In a few cases spring waters are met with which contain considerable quantities of lithium salts. Thus, W. A. Miller found as much as 0.372 gramme of lithium chloride in 1 litre of the water of a spring near Redruth in Cornwall.

Mode of Formation.—Lithium is obtained by the electrolytic decomposition of the fused chloride. For this purpose the dry salt is heated in a porcelain crucible, when it melts at a low red heat to a mobile liquid. A rod of *gas carbon* is made the positive electrode ; and a stout iron wire, one end of which is flattened out, is used for the negative pole, upon which the lithium is collected. On passing an electric current through the molten chloride, the metal forms as a bright globule upon the negative electrode. The wire is withdrawn and quickly dipped beneath petroleum, and the solidified globule of lithium is then cut off with a knife. The reduced metal, in its passage from the crucible to the petroleum, is protected from oxidation by the film of fused chloride which coats it.

Properties.—Lithium is a soft, silver-white metal, which soon tarnishes on exposure to the air. It is easily cut with a knife, being softer than lead, but harder than sodium. It may be pressed into wire, and two pieces of the metal may be made to adhere, or welded together, at the ordinary temperature. Lithium is the lightest known solid, its specific gravity being 0.59. Its extreme lightness is illustrated by the fact that the metal floats upon petroleum, a liquid which itself floats upon water. Lithium melts at 180°, and at a higher temperature it takes fire and burns with a bright white light. Lithium decomposes water at the ordinary temperature, liberating hydrogen and forming lithium hydroxide, LiHO; but when a fragment of the metal is thrown upon cold water it does not melt, and even with boiling water the action is not attended by inflammation of the hydrogen.

When strongly heated in nitrogen the two elements unite, with feeble combustion, forming lithium nitride, NLi_3.

Lithium Oxide, Li_2O, is formed when the metal burns in the air. It is also obtained by heating the nitrate. It dissolves in water, forming lithium hydroxide, LiHO.

Lithium Hydroxide is produced by the prolonged boiling of lithium carbonate with milk of lime, the carbonate of this metal, unlike potassium and sodium carbonates, being only very slightly soluble in water.

Lithium Carbonate, Li_2CO_3, is obtained as a white precipitate when a solution of either potassium, sodium, or ammonium carbonate is added to a solution of either chloride or nitrate of lithium. The compound is only slightly soluble in cold water, 100 parts of water at 13° dissolving 0.77 part of the carbonate.

Lithium Phosphate, Li_3PO_4, is precipitated as a crystalline powder, by the addition of hydrogen disodium phosphate to a solution of a lithium salt. In the presence of sodium hydroxide the precipitation is complete, and the formation of this compound is employed as a quantitative method for estimating lithium. The crystals contain $2H_2O$, which they lose when heated. Lithium phosphate is soluble in nitric, hydrochloric, and phosphoric acids, and from the latter solution, on evaporation, the dihydrogen phosphate is deposited (H_2LiPO_4) as deliquescent and very soluble crystals. The chloride, nitrate, and sulphate of lithium are obtained by dissolving the carbonate in the respective acids. The salts are readily soluble in water.

Rubidium and Caesium.*—These two rare elements, which were first discovered by Bunsen in the waters of Dürkheim, in the years 1860–61, are met with, associated with sodium and potassium, in certain minerals, such as lepidolites (lithium mica), porphyrites, and in carnallite. They are also found

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* For detailed descriptions of these elements and their compounds, the student is referred to larger works.

in many mineral waters, in the mother-liquors from the evaporation of sea-water, and in the ashes of plants. Although widely distributed, the quantities present are extremely minute, one of the richest lepidolites in which these metals occur containing only 0.24 per cent. of rubidium oxide.

The rare mineral *pollux*, a silicate of aluminium and caesium, containing also iron calcium and sodium, is the only known mineral in which either of these two elements occurs as an essential constituent. The analysis of Pisani (1864) gives 34.07 per cent. of caesium oxide in this substance.

Rubidium is obtained by heating the carbonate with carbon (the charred tartrate), as in the older method for the preparation of sodium and potassium.

Caesium cannot be isolated by this reaction, but is obtained by the electrolysis of the fused cyanide, Cs(CN) (mixed with barium cyanide in order to render it more readily fusible). Rubidium melts at 38.5°, caesium at 26.5°.

Rubidium gives a green vapour, and when sublimed in a vacuous tube yields a thin film of metal, which appears deep blue by transmitted light: when slowly sublimed in this way the metal forms small needle-shaped crystals. The compounds of these metals closely resemble those of potassium, from which they can only be distinguished by the different spectra they give.

AMMONIUM SALTS.

The monovalent group or radical (NH_4) is capable of replacing one atom of hydrogen in acids, thereby giving rise to a series of salts which are closely analogous to, and are isomorphous with, those of potassium. The radical (NH_4), to which the name *ammonium* is given, has never been isolated. United to an atomic electric charge it constitutes the anion $NH_4^{\cdot}$, ammonion, which closely resembles sodion and potassion. When an amalgam of sodium and mercury is thrown into a solution of ammonium chloride, the mercury swells up into a honeycombed or sponge-like mass, which floats upon the surface of the liquid. This so-called ammonium amalgam was at one time thought to be a true amalgam of mercury with the metallic radical ammonium. It is now generally believed to consist of mercury which is simply inflated by the evolution of hydrogen and ammonia gas. When this sponge-like substance is subjected to changes of pressure, it is found to contract and expand in conformity to Boyle's law: its formation may be represented by the equation—

$$Hg_xNa_y + yNH_4Cl = yNaCl + xHg + yNH_3 + yH.$$

In the course of a few minutes the inflated mass shrinks down, and ordinary mercury remains at the bottom of the solution, hydrogen and ammonia having been rapidly evolved.

The ammonium salts are obtained for the most part from the *ammoniacal liquor* of the gasworks. The material is treated with lime, and distilled ; and the ammonia so driven off is absorbed in sulphuric or hydrochloric acid, giving rise to ammonium sulphate or chloride.

Ammonium Chloride (*sal ammoniac*), NH_4Cl.—The product obtained by absorbing ammonia from gas liquor in hydrochloric acid is purified by sublimation. The crude material is heated in large iron pots, covered with iron dome-shaped vessels, into which the substance sublimes. Ammonium chloride crystallises in arborescent or fern-like crystals (Fig. 141), consisting of groups of small octahedra belonging to the regular system.

FIG. 141.

100 parts of water at 10° dissolve 32.8 parts, and at 100°, 77 parts of the salt. On boiling the aqueous solution, dissociation to a small extent takes place, and a portion of the ammonia escapes with the steam ; the solution at the same time becoming slightly acid.

Ammonium Sulphate $(NH_4)_2SO_4$.—The product obtained by the absorption of ammonia obtained from gas liquors by sulphuric acid is purified by recrystallisation, when it forms colourless rhombic crystals, isomorphous with potassium sulphate. 100 parts of water at the ordinary temperature dissolve 50 parts of the salt. The chief use of ammonium sulphate is for agricultural purposes, as a manure; and for this use the crude salt, as first obtained, which is usually more or less coloured with tarry matters, is employed. Ammonium sulphate is also used for the preparation of ammonia alum and other ammonium compounds, as well as in the ammonia-soda process.

Ammonium Carbonates.—Commercial ammonium carbonate (*sal volatile*) is obtained by heating a mixture of ammonium sulphate and ground chalk to redness in horizontal iron retorts or cylinders, and conducting the vapours into leaden receivers or chambers, where the carbonate condenses as a solid crust. It is afterwards purified by resublimation, when it is obtained as a white fibrous mass. This substance is a mixture of hydrogen ammonium carbonate, $H(NH_4)CO_3$, and ammonium carbamate, $(NH_4)CO_2(NH_2)$, and smells strongly ammoniacal. When treated with alcohol the ammonium carbamate is dissolved, leaving the carbonate behind.

Normal Ammonium Carbonate, $(NH_4)_2CO_3$, is obtained from the commercial compound, by passing ammonia gas into a strong aqueous solution, or by digesting the compound in strong aqueous ammonia. The carbamate present is converted into normal carbonate by the action of the water, thus—

$$(NH_4)CO_2(NH_2) + H_2O = (NH_4)CO_3(NH_4) = (NH_4)_2CO_3\,;$$

and the ammonia converts the bicarbonate into the normal salt, thus—

$$H(NH_4)CO_3 + NH_3 = (NH_4)_2CO_3.$$

Normal ammonium carbonate on exposure to the air gives off ammonia, and passes back into hydrogen ammonium carbonate. When heated to 60° the salt breaks up into carbon dioxide, ammonia, and water.

Hydrogen Ammonium Carbonate, $H(NH_4)CO_3$, may also be obtained by passing carbon dioxide into a solution of the normal salt—

$$(NH_4)_2CO_3 + CO_2 + H_2O = 2H(NH_4)CO_3.$$

It forms large lustrous crystals belonging to the orthorhombic system, which, when dry, do not smell of ammonia. 100 parts of water at 15° dissolve 12.5 parts of this salt. At ordinary temperatures this solution on exposure to the air slowly gives off carbon dioxide, and becomes alkaline; and when heated above 36° the liquid begins to effervesce, owing to the rapid evolution of carbon dioxide. This salt forms with the normal carbonate a double salt analogous to sodium sesquicarbonate, and having the composition $(NH_4)_2CO_3,2H(NH_4)CO_3,H_2O$.

Ammonium Thiocyanate, $NH_4S(CN)$, is prepared by adding aqueous ammonia to an alcoholic solution of carbon disulphide, and allowing the mixture to stand, when ammonium thiocarbonate is formed, thus—

$$6NH_3+3H_2O+3CS_2=2(NH_4)_2CS_3+(NH_4)_2CO_3.$$

On heating this solution, the ammonium thiocarbonate is decomposed with evolution of sulphuretted hydrogen—

$$(NH_4)_2CS_3=2H_2S+NH_4S(CN).$$

Ammonium thiocyanate (known also as *ammonium sulphocyanate*) forms colourless crystals, which are extremely soluble both in water and alcohol. The solution in water is attended with considerable absorption of heat: thus, if 20 grammes of the salt be dissolved in 25 cubic centimetres of water at 18°, the temperature of the liquid falls to $-13°$.

CHAPTER V

THE ELEMENTS OF GROUP I. (FAMILY B.)

Copper, Cu	63.6
Silver, Ag	107.93
Gold, Au	197.2

THE elements of this family present many striking contrasts to those of the other family belonging to the first group. These three metals are not acted upon by oxygen, or by water, at ordinary temperatures ; they are all found native in the uncombined state, and on this account are amongst the earliest metals known to man. The alkali metals, on the other hand, are instantly oxidised on exposure to air, they decompose water at the ordinary temperature, are never found native, and are amongst the most recently discovered metals. With the exception of sodium and potassium, which are used in a few manufacturing processes, the alkali metals, as such, are of little practical service to mankind, whilst the metals of this family are amongst the most useful of all the metals, and are the three universally adopted for coinage. Many of the compounds of the elements of this family are similarly constituted to those of the alkali metals : thus, with oxygen and with sulphur we have Cu_2O, Ag_2O, Au_2O, and Cu_2S, Ag_2S, Au_2S, corresponding to Li_2O and K_2S.

With the halogens they all form compounds of the type RX. Although the three elements, copper, silver, and gold, fall into the same family upon the basis of the periodic classification of the elements, they are in many respects widely dissimilar. Thus, silver is consistently monovalent, while copper is divalent, forming compounds of the type CuX_2, and gold is trivalent, giving compounds AuX_3. The chlorides, AgCl and Cu_2Cl_2, on the other hand, are both insoluble in water, are both soluble in ammonia, and both absorb ammonia.

In many of their physical attributes, these metals show a regular gradation in their properties. Thus, as regards malleability and ductility, silver is intermediate between copper and gold, the latter possessing these properties in the highest degree. With respect to their tenacity, silver is again intermediate, copper being the most, and gold the least tenacious of the three.

COPPER.

Symbol, Cu. Atomic weight=63.6.

Occurrence.—Copper is found in the elementary condition in various parts of the world, notably in the neighbourhood of Lake Superior, where native copper occurs in enormous masses. In combination, copper is a very abundant element, and is widely distributed, the most important of these natural compounds being the following—

Ruby ore	Cu_2O.	Purple copper ore	$3Cu_2S,Fe_2S_3$ or Cu_3FeS_3.
Copper glance	Cu_2S.	Malachite	$CuCO_3,Cu(HO)_2$.
Copper pyrites	Cu_2S,Fe_2S_3 or $CuFeS_2$.	Azurite	$2CuCO_3,Cu(HO)_2$.

Modes of Formation.—The methods by which copper is obtained from its ores vary with the nature of the ore. From ores containing no sulphur, such as the carbonates and oxide, the metal may be obtained by a method known as the *reducing process*, which consists in smelting down the ore in a blast-furnace with coal or coke, when the metal is reduced according to the equation—

$$Cu_2O + C = CO + 2Cu.$$

In the case of mixed ores, containing sulphides, the process (known as the English method) consists of six distinct stages—

(1.) The ores, which contain on an average 30 per cent. of iron and 13 of copper (the remainder being chiefly sulphur and silica), are first calcined; usually in a reverberatory furnace, whereby a portion of the sulphur is burnt to sulphur dioxide, and the metals are partially oxidised.

(2.) The second step consists in fusing the calcined ore; when the copper oxides, formed during calcination, react upon a portion of the ferrous sulphide, with the formation of cuprous sulphide and ferrous oxide, thus—

$$Cu_2O + FeS = Cu_2S + FeO.$$
$$2CuO + 2FeS = Cu_2S + 2FeO + S.$$

The oxide of iron combines with the silica already present (or which is added in the form of *metal-slag* obtained from the fourth step) to form a fusible silicate of iron, or slag, which contains little or no copper. This is run off, and a fused regulus remains, consisting of cuprous and ferrous sulphides, known as *coarse-metal*, and containing from 30 to 35 per cent. of copper. This molten regulus, which has a composition very similar to copper pyrites, is usually allowed to flow into water, whereby it is obtained in a granulated condition favourable for the next operation.

(3.) The third step consists in calcining the granulated coarse-metal ; the result, as in the first calcination, being the removal of a part of the sulphur as sulphur dioxide, and the partial oxidation of the metals.

(4.) The calcined mass is next fused along with *refinery-slag*, which results in the production of a regulus consisting of nearly pure cuprous sulphide, the greater part of the iron having passed into the slag (known as *metal-slag*). This regulus, called *fine-metal*, or *white-metal*, contains from 60 to 75 per cent. of copper.

(5.) The fifth operation consists in roasting the "white-metal" in a reverberatory furnace. A portion of the cuprous sulphide is here oxidised into cuprous oxide, which, as the temperature rises, reacts upon another portion of cuprous sulphide, thus—

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

At the same time any remaining ferrous sulphide is converted into oxide, thus—

$$3Cu_2O + FeS = 6Cu + FeO + SO_2.$$

The metallic copper so obtained presents a blistered appearance, and on this account is known as *blister-copper.*

(6.) This impure copper is lastly subjected to a refining process. For this purpose it is melted down upon the hearth of a reverberatory furnace, in an oxidising atmosphere. The impurities present in the metal, such as iron, lead, and arsenic, are the first to oxidise ; and the oxides either volatilise or combine with the siliceous matter of which the furnace bed is composed, forming a slag, which is removed. The oxidation is continued until the copper itself begins to oxidise, when the oxide so formed reacts upon any remaining cuprous sulphide with the reduction of copper and the evolution of sulphur dioxide, according to the above equation. The metal at this stage is termed *dry copper ;* and in order to reduce the copper oxide which it still contains, the molten mass is stirred with poles of wood, and a quantity of anthracite is thrown upon the surface to complete the reducing process.

Wet Process.—Copper is extracted from the burnt pyrites, obtained in enormous quantities in the manufacture of sulphuric acid, which contains about 3 per cent. of copper. Although too poor in copper to be submitted to the smelting process, it is found that when calcined with 12 to 15 per cent. of common salt, the copper is all converted into cupric chloride. On lixiviating the calcined mass with water, the cupric chloride goes into solution, and metallic copper can be precipitated from it by means of scrap-iron or by electrolysis.

Properties.—Copper is a lustrous metal, having a characteristic reddish-brown colour. The peculiar copper-red colour of the metal is best seen by causing the light to be several times reflected from the surface before reaching the eye.

Native copper is occasionally found crystallised in regular octahedra, and small crystals of the same form may be artificially obtained by the slow deposition of the metal from solutions of its salts by processes of reduction.

Copper is an extremely tough metal, and admits of being drawn into fine wire, and hammered out into thin leaf. Its ductility and malleability are greatly diminished by admixture with even minute quantities of impurities. When heated nearly to its melting-point, copper becomes sufficiently brittle to be powdered. The specific gravity of pure copper, electrolytically deposited, is 8.945, which by hammering is increased to 8.95.

Copper is only slowly acted upon by exposure to dry air at ordinary temperatures; but in the presence of atmospheric moisture and carbon dioxide it becomes coated with a greenish, basic carbonate. When heated in air or oxygen, it is converted into black cupric oxide, which flakes off the surface in the form of scales. When volatilised in the electric arc, copper gives a vapour having a rich emerald-green colour.

Copper is readily attacked by nitric acid, either dilute or concentrated, with the formation of copper nitrate and oxides of nitrogen (page 246).

Dilute hydrochloric and sulphuric acids are without action upon copper when air is excluded, but slowly attack it in the presence of air, or in contact with platinum. Cold concentrated sulphuric acid does not act upon copper; but when heated, copper sulphate and sulphur dioxide are formed, with the simultaneous production of varying quantities of cuprous and cupric sulphides, which remain as a black residue (page 416).

Finely divided copper is slowly dissolved by boiling concentrated hydrochloric acid, with evolution of hydrogen and formation of cuprous chloride—

$$2Cu+2HCl=Cu_2Cl_2+H_2 \text{ or}$$
$$2Cu+2H^{\cdot}+2Cl'=2Cu^{\cdot}+2Cl'+H_2.$$

In the presence of air, copper is acted upon by a solution of ammonia, the oxide dissolving in the ammonia forming a deep blue solution.

Copper is an extremely good electric conductor, being only second to silver in this respect; it is therefore extensively employed for cables, or leads, for purposes of telegraphy and electric lighting.

Copper possesses the property, in a high degree, of being deposited in a coherent form by the electrolysis of solutions of its salts. On this account it is extensively used in processes of electrotyping.

Alloys of Copper.—The most extensive use of copper is in the formation of certain alloys, many of which are of great technical value. The following are among the most important :—

English brass . . .	Copper 2 parts	Zinc	1 part
Dutch brass (*Tombac*) .	„ 5 „	„	1 „
Muntz metal . . .	„ 3 „	„	1 „
Gun metal . . .	„ 9 „	Tin	1 „
Aluminium bronze . . .	„ 9 „	Aluminium	1 „

Oxides of Copper.—Two oxides of copper are well known, namely, cuprous oxide (*copper sub-oxide*), Cu_2O, and cupric oxide (*copper monoxide*), CuO.

Cuprous Oxide, Cu_2O, occurs native as *red copper ore.* It is formed when finely divided copper is gently heated in a current of air, or when a mixture of cuprous chloride and sodium carbonate is gently heated in a covered crucible.

$$Cu_2Cl_2+Na_2CO_3=2NaCl+CO_2+Cu_2O.$$

Cuprous oxide is also obtained when an alkaline solution of a copper salt is reduced by grape sugar.

Cuprous oxide is insoluble in water; it is converted into cuprous chloride by strong hydrochloric acid. Nitric acid converts it into cupric nitrate with the evolution of oxides of nitrogen. When acted upon by dilute sulphuric acid, it is partly reduced to metallic copper and partly oxidised into copper sulphate, thus—

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

When heated with the strong acid it is entirely oxidised, thus—

$$Cu_2O + 3H_2SO_4 = 2CuSO_4 + SO_2 + 3H_2O.$$

Cuprous oxide fuses at a red heat, and when melted with glass, imparts to the latter a rich ruby-red colour.

Cupric Oxide, CuO, occurs as the rather rare mineral, *tenorite.* It is formed when copper is strongly heated in the air or in oxygen, or by gently igniting either the nitrate, carbonate, or hydroxide. It is a black powder, which rapidly absorbs moisture from the air. When heated, it first cakes together and finally fuses, giving up a part of its oxygen, and leaving a residue consisting of $CuO,2Cu_2O$.

When heated in a stream of carbon monoxide, marsh gas, or hydrogen, it is reduced to the metallic state. Similarly, when mixed with organic compounds containing carbon and hydrogen, it oxidises these elements to carbon dioxide and water, itself being reduced: on this property depends its use in the ultimate analysis of organic compounds.

Cupric Hydroxide, $Cu(HO)_2$, is the pale blue precipitate produced when sodium or potassium hydroxide is added in excess to a solution of a copper salt. The compound, when washed, may be dried at 100° without parting with water; but if the liquid in which it is precipitated be boiled, the compound blackens, and is converted into a hydrate having the composition $Cu(HO)_2,2CuO$. Cupric hydrate dissolves in ammonia, forming a deep blue liquid, which possesses the property of dissolving cellulose (cotton wool, filter paper, &c.).

Salts of Copper.—Copper forms two elementary ions, monocuprion $Cu^{\cdot}$ and dicuprion $Cu^{\cdot\cdot}$, giving rise to two series of salts, namely, *cuprous* and *cupric* salts. The former, which are colourless, readily pass by oxidation into cupric salts, and serve therefore as powerful reducing agents, and are mostly insoluble in water. The cupric salts in the hydrated condition are either blue or green in colour; the anhydrous cupric salts are colourless or yellow. The normal salts are mostly soluble in water. Copper salts impart to a non-luminous flame a blue or green colour, and on this account are employed in pyrotechny. The soluble salts are poisonous.

Cuprous Chloride, Cu_2Cl_2, may be obtained by dissolving cuprous oxide in hydrochloric acid. It is more readily prepared by boiling a solution of cupric chloride in hydrochloric acid, with copper turnings or foil. The nascent hydrogen, liberated by the action of the hydrochloric acid upon the copper, reduces the cupric chloride to cuprous chloride. The liquid is then poured into water, which causes the precipitation of the cuprous chloride as a white crystalline powder.

A mixture of zinc dust and copper oxide added to strong hydrochloric acid also yields cuprous chloride, the nascent hydrogen in this case being derived from the action of the acid upon the zinc, and this causes the reduction of cupric chloride formed by the action of the acid upon the cupric oxide.

Cuprous chloride melts when heated, and volatilises without decomposition. It is insoluble in water, but dissolves in hydrochloric acid, ammonia, and alkaline chlorides. These solutions, on exposure to the air, absorb oxygen, turning first brown, and finally depositing a greenish-blue precipitate of copper oxychloride, $CuCl_2,3CuO,4H_2O$. This compound occurs native as the mineral *atacamite.* Solutions of cuprous chloride also absorb carbon monoxide, forming a crystalline compound, believed to have the composition, $COCu_2Cl_2,2H_2O$. They also absorb acetylene (see page 318).

Cuprous bromide, Cu_2Br_2; iodide, Cu_2I_2; and fluoride, Cu_2F_2, are also known.

Cupric Chloride, $CuCl_2$.—This compound is formed when copper is dissolved in nitro-hydrochloric acid, or when cupric oxide, carbonate, or hydroxide are dissolved in hydrochloric acid. It is also produced when copper is burnt in chlorine.

Cupric chloride is readily soluble in water, forming a deep green solution, which, on being largely diluted, turns blue. The salt crystallises in green rhombic prisms, with $2H_2O$. When heated it loses its water, and at a dull red heat is converted into cuprous chloride, with evolution of chlorine (see page 355).

Cupric chloride forms three compounds with ammonia. The anhydrous salt absorbs ammonia gas, forming a blue compound, $CuCl_2,6NH_3$. When ammonia is passed into aqueous cupric chloride, the solution deposits deep blue crystals (tetragonal pyramids) of the compound, $CuCl_2,4NH_3,H_2O$. Both these substances, when moderately heated, yield the green compound $CuCl_2,2NH_3$, which at a higher temperature is decomposed, thus—

$$6(CuCl_2,2NH_3)=3Cu_2Cl_2+6NH_4Cl+4NH_3+N_2.$$

Cupric bromide, $CuBr_2$, and fluoride, CuF_2, are known, but the iodide is unknown.

Cupric Nitrate, $Cu(NO_3)_2,3H_2O$, may be obtained by the action of nitric acid upon cupric oxide, hydroxide, carbonate, or the metal itself. It is deposited from the solution in deep blue deliquescent crystals, soluble in alcohol. When heated to about 65° the crystals lose nitric acid and water, and are converted into the basic nitrate, $Cu(NO_3)_2,3Cu(HO)_2$. The normal salt, therefore, cannot be obtained anhydrous. Cupric nitrate is a caustic, powerfully oxidising substance. If the moist salt be rubbed in a mortar with a quantity of tinfoil, the tin is quickly converted into oxide, with considerable rise of temperature. When a solution containing copper nitrate and ammonium nitrate is evaporated, the mixture suddenly deflagrates when a certain degree of concentration is reached.

Cupric Sulphate (*blue vitriol*), $CuSO_4,5H_2O$, is the most important of all the copper salts. It is formed when either the metal or the oxide is dissolved in sulphuric acid. On a commercial scale it is obtained from waste copper by first converting the metal into sulphide by heating it in a furnace, and throwing sulphur upon the red-hot metal. Air is then admitted, and the sulphide is thereby oxidised into sulphate, which is dissolved in water and crystallised.

It is also manufactured from the sulphur ores of copper, by roasting them under such conditions that the iron is for the most part converted into oxide, while the copper is oxidised to sulphate. On lixiviating the roasted mass the copper sulphate, with a certain amount of ferrous sulphate, is dissolved out. The ores may also be roasted so as to convert both the metals into oxides; the mass is then treated with "chamber acid," which dissolves copper oxide, leaving the iron oxide for the most part unacted upon.

Cupric and ferrous sulphates cannot be entirely separated by crystallisation, as a solution of these salts deposits a double sulphate of the two metals. If, however, the amount of iron present is comparatively small, the first crop of crystals obtained is moderately pure copper sulphate. The copper is removed from the mother-liquors by precipitation upon plates of iron, and the copper so obtained is converted into sulphide, as above described.

Copper sulphate forms large blue asymmetric (*triclinic*) crystals, with $5H_2O$. At 100° it is converted into a bluish-white salt, $CuSO_4,H_2O$, and at 220° to 240° it becomes anhydrous. The anhydrous salt is white, and extremely hygroscopic, and is used both for the detection and removal of small quantities of water in organic liquids.

100 parts of water at 10° dissolve 36.6 parts, and at 100°, 203.3 parts of the crystallised salt.

Several basic sulphates of copper are known: thus, when the normal salt is submitted to prolonged heating, it is converted into an amorphous yellow powder, consisting of $CuSO_4,CuO$, which when thrown into cold water forms an insoluble green compound, $CuSO_4,3Cu(HO)_2$, and on treatment with boiling water yields $CuSO_4,2Cu(HO)_2$. Copper sulphate forms several compounds with ammonia. Thus, the anhydrous salt readily absorbs ammonia gas, forming the compound, $CuSO_4,5NH_3$. When excess of ammonia is added to a solution of copper sulphate, the deep blue solution deposits blue crystals of $CuSO_4,H_2O,4NH_3$. At 150° this compound is converted into $CuSO_4,2NH_3$, and at 200° it loses one more molecule of ammonia, leaving $CuSO_4,NH_3$.

Cupric Carbonates.—The normal carbonate has not been obtained. The two most important basic carbonates are (1) $CuCO_3,Cu(HO)_2$, occurring native as *malachite*, and obtained when sodium carbonate is added to a solution of copper sulphate (the green deposit which appears upon copper when exposed to atmospheric moisture and carbon dioxide (*verdigris*) is the same compound); and (2) $2CuCO_3,Cu(HO)_2$, occurring as the mineral *azurite*.

Sulphides of Copper.—Two sulphides are known, corresponding to the two oxides.

Cuprous Sulphide, Cu_2S, occurs in nature as *copper glance*, in the form of grey metallic-looking rhombic crystals. It is produced when copper burns in sulphur vapour, or when an excess of copper filings is heated with sulphur.

Cupric Sulphide, CuS, is met with in nature as the mineral *indigo-copper*. It is obtained when either copper or cuprous sulphide is heated with sulphur to a temperature not beyond 114°; so obtained, the compound is blue. As a black precipitate, it is formed when sulphuretted hydrogen is passed into solutions of cupric salts.

SILVER.

Symbol, Ag. Atomic weight = 107.93.

Occurrence.—Silver is found uncombined, occasionally in masses weighing several cwts. Such native silver usually contains copper, gold, and other metals.

Amongst the more important natural compounds of silver are the following :—

Argentite, or *silver glance*	Ag_2S.
Pyrargyrite, or *ruby silver ore*	$3Ag_2S,Sb_2S_3$, or Ag_3SbS_3.
Proustite, or *light red silver ore*	$3Ag_2S,As_2S_3$ „ Ag_3AsS_3.
Stephanite	$5Ag_2S,Sb_2S_3$ „ Ag_5SbS_4.
Polybasite	$9(Ag_2S,Cu_2S),Sb_2S_3,As_2S_3$.
Stromeyerite	Ag_2S,Cu_2S.
Horn silver	$AgCl$.

Silver is present also in most ores of lead, notably with *galena* (lead sulphide); argentiferous lead ores constituting one of the main supplies of silver.

Modes of Formation.—This element may be obtained from its salts by the electrolysis of their aqueous solutions. The metal is so readily reduced from its compounds, that many organic substances, such as grape sugar, aldehyde, certain tartrates, &c., are capable of effecting its deposition. When a strip of zinc is introduced into silver nitrate solution, the silver is at once deposited upon the zinc as a crystalline mass.

Pure silver for analytical purposes may be prepared by precipitating silver chloride, by the addition of hydrochloric acid to a solution of the nitrate, and reducing the chloride by boiling with sodium hydroxide and sugar, or by means of metallic zinc. In this way the metal is obtained as a fine grey powder. The chloride may also be reduced by fusion with sodium carbonate, when the silver is obtained as a button at the bottom of the crucible. The methods by which silver is obtained from its ores are very varied; they may, however, be classed under three heads, namely—

1. Processes involving the use of mercury. (Amalgamation processes.)
2. Processes by means of lead.
3. Wet processes.

(1.) **Amalgamation Processes.**—These depend upon the fact that certain compounds of silver are reduced by mercury. The reduced silver then dissolves in the mercury, forming an amalgam, from which the silver is obtained, and the mercury recovered by distillation. The process, as still carried on in Mexico and South America, is the following. The ore is first crushed and then ground to a fine powder with water, and the mud so obtained is mixed with 3 to 5 per cent. of common salt, and spread upon the floor of a circular paved space, the mixing being effected by the treading of mules. After the lapse of a day, mercury is added, together with a quantity of roasted pyrites (known as *magistral*, and consisting of a crude mixture of cupric and ferric sulphates and oxides), and the materials thoroughly incorporated. Fresh mercury is added from time to time, during the several days required for the completion of the chemical decompositions that take place. The exact nature of these changes is not thoroughly understood, but it is probable that they involve first the formation of copper chlorides, by double decomposition between the copper sulphate and sodium chloride, and the subsequent action of these upon the silver sulphide present in the ore, thus—

$$2CuCl_2 + Ag_2S = 2AgCl + Cu_2Cl_2 + S.$$
$$Cu_2Cl_2 + Ag_2S = 2AgCl + Cu_2S.$$

The silver chloride dissolves in the sodium chloride present, and is reduced by the mercury, with the production of mercurous chloride (*calomel*), which is ultimately lost in the washing—

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag.$$

The amalgam is first washed, and freed from adhering particles of mineral, and is then filtered through canvas bags, whereby the excess of mercury is removed. The solid residue, containing the silver, is then submitted to distillation.

In other amalgamation processes the ore is first roasted with salt, in order to convert the silver into chloride. The roasted ore is reduced to fine powder with water, and introduced into revolving casks along with scrap iron, when the chloride is reduced according to the equation—

$$2AgCl + Fe = 2Ag + FeCl_2,$$

and the reduced silver is then extracted by the addition of mercury, with which it amalgamates.

In the modern amalgamation process the finely crushed ore, with water, is placed in iron pans provided with revolving machinery, which serves the purpose of further grinding, and also of mixing. When the ore is reduced to an almost impalpable powder, mercury is added, and the machinery is kept in operation for a few hours, when the amalgamation is complete; sometimes common salt and copper sulphate are added, either together or singly. Their presence does not appear to be necessary to the process, except in so far as they aid in keeping the surface of the mercury clean, or "quick"; for in the extremely finely divided condition to which the ore is reduced in this "pan" amalgamation process, the silver sulphide is readily acted upon by mercury, with the formation of mercuric sulphide—

$$Ag_2S + Hg = HgS + 2Ag,$$

and the silver so reduced dissolves in the excess of mercury, from which it is finally separated by distillation.

(2.) **Processes by Means of Lead.**—When silver ores are smelted with lead, or with materials which yield metallic lead; in other words, when silver ores are smelted with lead ores, an alloy of silver and lead is obtained, from which the silver can be separated. When the argentiferous lead is rich in silver, the alloy is submitted to *cupellation*, which consists in heating the metal in a reverberatory furnace, the hearth of which consists of a movable, oval-shaped, shallow dish, made of bone ash, known as a *cupel*, or *test*. The alloy is fed into this cupel from a melting-pot, and a blast of air is projected upon the surface of the molten metal. The lead is thus converted into litharge, and the melted oxide, by the force of the blast, is made to overflow into iron pots. As the oxidation of the lead reaches completion, the thin film of litharge begins to exhibit iridescent interference colours, which presently disappear, leaving the brilliant surface of the melted silver. The sudden appearance of the bright metallic surface is known as the *flashing* of silver.

In the case of argentiferous lead too poor in silver to be directly cupelled, the alloy is submitted to one of two processes of concentration, namely, the *Pattinson process*, or the *Parkes's process.*

The *Pattinson process* for desilverising lead depends upon the fact that alloys of silver and lead have a lower melting-point than pure lead, and therefore when argentiferous lead is melted and allowed to cool, the crystals which first form consist of lead which is nearly or quite pure, and the greater part of the silver is in the still liquid portion. The operation is carried out in a row of iron pots. A quantity of the metal is melted in one pot, and as it cools the crystals which begin to form are removed by means of a perforated iron ladle and transferred to the next pot on one side. This operation is continued until a definite proportion (either two-thirds or seven-eighths, depending upon the proportion of silver) has been removed. The residue is then transferred to the neighbouring pot on the opposite side, and a second charge melted up in the first pot. As the neighbouring pots fill up they are similarly treated, and in this way an alloy, gradually becoming richer and richer in silver, is passed along in one direction, and purer and purer lead is sent in the opposite way. The rich alloy is then cupelled.

The *Parkes's process* depends upon the fact that when zinc is added to a melted alloy of lead and silver, the zinc deprives the lead of the silver, and itself forms an alloy with it. The alloy of zinc and silver rises to the surface and is the first portion to solidify, and can be removed. The operation is carried out in iron pots. The argentiferous lead is melted and a quantity of zinc is thoroughly stirred into the molten mass, the amount of zinc depending upon the richness of the lead. As the mixture cools, the first portions to solidify are skimmed off with a ladle and transferred to another pot. These skimmings, consisting of zinc, silver, and lead, are first liquated ; that is, carefully heated to such a temperature that the adhering lead melts and flows away from the less fusible zinc silver alloy. The solid alloy is then distilled, and the residue, consisting of silver and lead, is submitted to cupellation.

(3.) **Wet Processes** (*Ziervogel process*).—When argentiferous pyrites, or an artificially formed regulus containing sulphides of silver, copper, and iron is roasted, the sulphides are first converted into sulphates ; and, as the roasting continues, first the iron, then the copper, and lastly the silver sulphate, is converted into oxide. By careful regulation the process is continued until the whole of the iron and a part of the copper sulphates are decomposed. On lixiviating the roasted mass with water, the silver sulphate, together with the remaining copper sulphate, dissolves. From this solution the silver is precipitated by scrap copper.

The copper is recovered from the solution by precipitation with iron.

The Percy-Patera Process.—In this method the ore is roasted with salt and the silver chloride so formed is then extracted by means of sodium thiosulphate—

$$Na_2S_2O_3 + AgCl = NaCl + NaAgS_2O_3.$$

To the solution so obtained sodium or calcium sulphide is added, which precipitates silver sulphide—

$$2NaAgS_2O_3 + Na_2S = Ag_2S + 2Na_2S_2O_3.$$

The silver sulphide is then reduced by being roasted in a reverberatory furnace.

FIG. 142.

Properties.—Silver is a lustrous white metal which appears yellow when the light is reflected many times from its surface before reaching the eye. It is unacted upon by atmospheric oxygen, but quickly becomes tarnished by traces of sulphuretted hydrogen in the air. Silver has the highest conductivity for heat and electricity of all the metals. It is extremely malleable and ductile, being second only to gold. Thin films of silver appear blue by transmitted light. Silver melts at about 1000°, and when heated by the oxyhydrogen flame may be readily made to boil and distil. The pure metal employed by Stas for the determination of the atomic weight was obtained by distillation in this way. When volatilised in the electric arc, the vapour of silver has a brilliant green colour. Molten silver absorbs as much as twenty-two times its volume of oxygen, which it gives up again (with the exception of 0.7 volume) on solidification. As the mass cools, the oxygen evolved often bursts through the outer crust of solidified metal with considerable violence, ejecting portions of the still liquid silver as irregular excrescences, as seen in Fig. 142. This phenomenon is known as the "spitting" of silver. Small quantities of admixed metals prevent the absorption of oxygen.

Silver is readily soluble in nitric acid, forming argentic nitrate, with liberation of oxides of nitrogen. Hot concentrated sulphuric acid converts it into argentic sulphate, with formation of sulphur dioxide (the reactions in both cases being similar to those with copper).

Silver Alloys.—Silver, alloyed with copper, is largely employed for coinage and for ornamental purposes. English *standard silver* contains 925 parts of silver per 1000. It is said, therefore, to have a *fineness* of 925. In France three standards are used. That for coinage contains 900 parts per 1000. For medals and plate the silver has a fineness of 950, while for jewellery it contains only 800 parts per 1000.

Silver-plating.—For purposes of electro-plating, a solution of silver cyanide in potassium cyanide is used. When a feeble electric current is passed through this solution (the article to be silvered being the negative electrode, and a plate of silver the positive), silver in a coherent form is precipitated upon the negative electrode, thereby coating the object; and cyanogen is disengaged at the positive pole, where it dissolves the electrode, reforming silver cyanide.

Silver is reduced from solutions and deposited as a coherent film by a variety of organic compounds; and various methods based upon this property are in use for obtaining mirrors and silvered glass specula for optical purposes. One such method is the following. Two solutions are prepared, thus—

(1.) Ten grammes of silver nitrate are dissolved in a small quantity of water, and ammonia added until the precipitate dissolves. The liquid is then filtered and diluted up to one litre.

(2.) Two grammes of silver nitrate are dissolved in a litre of boiling water, and 1.66 gramme of Rochelle salt (sodium potassium tartrate, $NaKC_4H_4O_6$) are added and the liquid filtered. Equal volumes of these two solutions are poured into a shallow dish, and the glass to be silvered (after being perfectly cleaned) is laid in the solution. In about twenty minutes the silver will have formed a brilliant mirror upon the glass.*

Oxides of Silver.—Three oxides are believed to exist, namely—

Silver monoxide	Ag_2O.
Silver peroxide	Ag_2O_2
Silver suboxide	Ag_4O?

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* By the reduction of silver solutions in the presence of certain organic compounds, Carey Lea has obtained the metal in the form of a dark bronze powder, which, when dry, resembles burnished gold. He has also obtained it exhibiting bluish-green and ruby-red colours. The material differs in many of its properties from ordinary silver, and is regarded by its discoverer as an allotropic form of silver (*American Journal of Science*, 1891).

Silver Monoxide (*argentic oxide*), Ag_2O, is obtained by adding sodium or potassium hydroxide to a solution of silver nitrate. A brown precipitate consisting of hydrated oxide is obtained which, when heated, is converted into the anhydrous compound. It is also formed when silver chloride is boiled with a strong solution of potassium hydroxide—

$$2AgCl + 2KHO = 2KCl + H_2O + Ag_2O.$$

Silver oxide is a black amorphous powder which, when heated to 260°, begins to give off oxygen, and become reduced to metallic silver. It is a powerful oxidising substance, and when rubbed with sulphur, red phosphorus, sulphides of antimony or arsenic, or other readily oxidised substances, it causes them to ignite.

Silver oxide, although only very slightly soluble in water (1 part in about 3000), imparts to the solution a distinct metallic taste and an alkaline reaction.

It is reduced by hydrogen at 100°, with formation of water and metallic silver; and when brought into contact with peroxide of hydrogen, oxygen is evolved and metallic silver formed (see p. 227).

Silver oxide is soluble in strong ammonia, and, on standing, the solution deposits black shining crystals of the so-called *fulminating silver*. When dry this compound is extremely explosive, and it often explodes when wet. Fulminating silver is believed to be the nitride, with the composition NAg_3.

Silver Peroxide, Ag_2O_2.—When a solution of silver nitrate is submitted to electrolysis, a black powder, consisting of small octahedral crystals, is deposited upon the positive electrode. The same compound is obtained when a plate of silver is made the positive electrode in the electrolysis of acidulated water, and also when silver is acted upon by ozone.

It readily parts with oxygen, and is a still more powerful oxidising agent than the monoxide. It dissolves in aqueous ammonia with the evolution of nitrogen—

$$3Ag_2O_2 + 2NH_3 = 3Ag_2O + 3H_2O + N_2.$$

Silver Suboxide, Ag_4O(?).—The black powder, obtained when silver citrate is reduced in a current of hydrogen at 100°, and potassium hydroxide is added to the aqueous solution of the residue, is believed to have the composition Ag_4O.

Silver Chloride, $AgCl$, is obtained as a white, bulky, curdy precipitate when a soluble chloride is added to silver nitrate. It melts at 451° to a yellowish liquid, which, on cooling, congeals to a tough horny mass (hence the name *horn silver*, as applied to the native silver chloride). The precipitated chloride is soluble to a slight extent in strong hydrochloric acid, but readily soluble in alkaline chlorides, in ammonia, and in sodium thiosulphate. Potassium cyanide converts silver chloride into silver cyanide, which dissolves in the excess of alkaline cyanide, forming the double cyanide KCN,AgCN. When exposed to the light, silver chloride darkens in colour, assuming first a violet tint, and finally becoming dark brown or black (see Photo-salts, p. 566).

Silver chloride absorbs large volumes of ammonia, forming the compound $2AgCl,3NH_3$ (see p. 275).

Silver Bromide, AgBr, is prepared similarly to the chloride, the precipitated compound having a pale yellow colour. It is less soluble in ammonia than silver chloride; in dilute ammonia it is nearly insoluble. Silver bromide is decomposed by chlorine, and at a temperature of 100° by hydrochloric acid. At ordinary temperatures this reaction is reversed, hydrobromic acid converting silver chloride into the bromide.

Dry silver bromide does not absorb gaseous ammonia. Silver bromide is extremely sensitive to the action of light, and is the chief silver compound used in dry-plate photography.

Silver Iodide, AgI, may be obtained by precipitation from silver nitrate, with a soluble iodide; or by dissolving silver in strong hydriodic acid. As obtained by precipitation it is an amorphous yellow substance, less soluble in ammonia than either the bromide or chloride. It dissolves in hot hydriodic acid, which on cooling deposits colourless crystals of AgI,HI; the addition of water to the solution precipitates the normal iodide, AgI. Silver iodide absorbs gaseous ammonia, forming a white compound, $2AgI,NH_3$, which, on free exposure to the air, evolves ammonia, and is reconverted into the yellow iodide.

Silver iodide is the most stable of the three halogen compounds. When either the chloride or bromide is treated with hydriodic acid or potassium iodide, iodine replaces the other halogens, forming silver iodide.

Silver Fluoride, AgF.—This compound is markedly different in many respects from the other halogen silver salts. It is obtained by dissolving silver oxide or carbonate in hydrofluoric acid, and is deposited from the solution in colourless, tetragonal pyramids, AgF,H_2O, or in prisms, $AgF,2H_2O$. The salt is extremely deliquescent, and very soluble in water. When dried in vacuo, the salt AgF,H_2O undergoes partial decomposition, leaving a brownish residue. When heated, it is partially decomposed, according to the equation—

$$2AgF,H_2O = 2Ag + 2HF + H_2O + O.$$

The dry salt absorbs gaseous ammonia in large quantities, more than 800 times its own volume being taken up by the powdered substance.

Silver Nitrate, $AgNO_3$, is obtained by dissolving silver in nitric acid. It forms large colourless rhombic tables, which melt at 218°, and resolidify to a white, fibrous, crystalline mass, known as *lunar caustic*. Below a red heat it gives off oxygen, and forms silver nitrite; and at higher temperatures it is decomposed into metallic silver and oxides of nitrogen. 100 parts of water at 0° dissolve 121.9 parts, and at 100°, 1110 parts of the crystallised salt; the solution is neutral. In contact with organic matter, silver nitrate is blackened on exposure to light. Thus, when the skin is touched with a solution of this salt, a few seconds' exposure to light causes a brown or black stain. Owing to this property, silver nitrate is employed for marking-inks. Silver nitrate absorbs gaseous ammonia, forming the compound $AgNO_3,3NH_3$, the absorption being accompanied with considerable rise of temperature. The compound $AgNO_3,2NH_3$ is deposited as rhombic prisms when aqueous silver nitrate is saturated with ammonia.

Silver Sulphate, Ag_2SO_4, is formed when silver, silver carbonate, or silver oxide is dissolved in sulphuric acid. It crystallises in rhombic prisms, isomorphous with sodium sulphate. With aluminium sulphate it forms an alum, in which the monovalent element silver takes the place of potassium in common alum, $Ag_2SO_4,Al_2(SO_4)_3,24H_2O$.

Photo-salts.—This name has been applied by Carey Lea to the coloured compounds formed by the action of light upon silver chloride, bromide, and iodide. The exact composition of the compounds that are formed when these silver salts are exposed to light is not definitely known. The change which they undergo has been attributed (1) to the partial reduction to metallic silver; (2) to the formation of sub-salts, such as Ag_2Cl, Ag_2Br, with elimination of chlorine or bromine; (3) to the formation of oxychloride or oxybromide; (4) to the production of double compounds of variable composition of the sub-salt with the normal salt.

GOLD.

Symbol, Au. Atomic weight = 197.2.

Occurrence.—This element occurs in nature almost exclusively in the uncombined condition, chiefly in quartz veins and in alluvial deposits formed by the disintegration of auriferous rocks. It is present in small quantities in many specimens of iron pyrites, copper pyrites, and many lead ores, from which it is often profitably extracted.

Gold is also met with in the form of an amalgam, and in combination with the element tellurium in the minerals *petzite*, $(AgAu)_2Te$, and *sylvanite*, $(AgAu)Te_2$.

Extraction.—Gold is extracted from auriferous quartz by causing the finely-crushed substance to flow, by means of a stream of water, over amalgamated copper plates. The gold particles adhere to the mercury, with which they amalgamate, and the amalgam so obtained is carefully removed and distilled.

From alluvial deposits, the native gold is separated by mechanical washing.

Gold is extracted from auriferous pyrites by means of chlorine. The ore is first carefully roasted, and, after being wetted, is exposed to the action of chlorine gas. The gold is thereby converted into the soluble auric chloride, $AuCl_3$, which is extracted by lixiviation, and precipitated by the addition of ferrous sulphate—

$$2AuCl_3 + 6FeSO_4 = 2Au + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

Native gold usually contains silver, from which it may be separated by passing chlorine over the molten metal, in crucibles glazed with borax. The fused chloride of silver rises to the surface, and is prevented from volatilising by a covering of melted borax. When the operation is complete, the crucible is allowed to cool, when the gold solidifies, and the still liquid silver chloride is poured off.

The Cyanide Process.—Increasing quantities of gold are at the present time extracted by solution in potassium cyanide. The method is specially advantageous in cases where the gold is present in the ore in a very finely divided condition, and it also possesses the advantage over the "chlorination process," that the preliminary operation of roasting is obviated. The crushed ore is treated with a dilute solution of potassium cyanide (containing from 0.25 to

1 per cent. of potassium cyanide), with free exposure to the atmosphere, since it has been shown that atmospheric oxygen takes a necessary part in the action. The gold is dissolved in the form of a double cyanide, according to the equation—

$$4Au+8KCy+2H_2O+O_2=4KHO+4KAuCy_2.$$

From this solution the gold is precipitated either by means of metallic zinc (usually in the form of fine turnings) or by electrolytic deposition. The precipitation by means of zinc takes place according to the equation—

$$2KAuCy_2+Zn=K_2ZnCy_4+2Au.$$

The deposit, after being freed as far as possible from zinc, is melted down with a suitable flux, and yields an alloy containing 70 to 80 per cent. of gold.

When the gold is precipitated electrolytically, the anodes employed are of lead foil. These are finally melted down and cupelled, yielding gold of a high degree of purity.

Properties.—Gold is a soft yellow metal, which, when seen by light many times reflected from its surface, appears red. It is not acted upon by air or oxygen at any temperature, and does not decompose steam. No single acid is capable of attacking it (except selenic acid); but it is dissolved by aqua-regia, with formation of auric chloride. Gold is the most malleable and ductile of all the metals, and when beaten into very thin leaf, it appears green by transmitted light.

Gold is most easily reduced from its combinations. Most metals, when placed in a solution of a gold salt, precipitate the gold, and the most feeble reducing agents bring about the same result. On this account a solution of auric chloride is used for *toning* photographs. All the compounds of gold, when ignited in the air, are reduced to metallic gold. Gold is readily deposited upon other metals by the process of electro-gilding, the most suitable solution being that of the double cyanide of gold and potassium, $Au(CN)_3,KCN$.

Gold Alloys.—Alloys of gold with copper and with silver are used for coinage and for ornamental purposes, pure gold being too soft for these purposes. Silver gives the alloy a paler colour than that of pure gold, while copper imparts to it a reddish tinge. The alloy used for English gold coin consists of gold, 11 parts; copper, 1 part. The proportion of gold in alloys is usually expressed in parts per 24 (instead of in percentages), these parts being termed *carats*. Thus, pure gold is said to be 24-carat gold; 18-carat gold contains, therefore, 18 parts of gold and 6 parts of copper or silver. Most countries have their own legal standards. In England the legal standard for gold coinage is 22-carats.

Compounds of Gold.—Gold forms two series of compounds, namely, *aurous*, in which the metal is monovalent, and *auric*, in which it is trivalent.

The composition of aurous compounds corresponds to that of the silver compounds. They are very readily decomposed. Thus, aurous chloride cannot exist in the presence of water, being decomposed into auric chloride and metallic gold. For this reason, when aurous oxide, Au_2O, is acted upon by aqueous hydrochloride acid it forms auric, and not aurous chloride, thus—

$$3Au_2O+6HCl=2AuCl_3+3H_2O+4Au.$$

With iodine gold forms only aurous iodide, AuI; therefore, when auric oxide is acted upon by hydriodic acid, aurous iodide and free iodine are formed, thus—

$$Au_2O_3+6HI=2AuI+2I_2+3H_2O.$$

Auric Chloride, $AuCl_3$, is obtained by dissolving gold in aqua-regia, and evaporating the solution to dryness. When the residue is dissolved in water the concentrated solution deposits reddish crystals of the composition $AuCl_32H_2O$. These lose their water when carefully heated, leaving a brown mass of deliquescent crystals. Auric chloride forms double chlorides with the alkaline chlorides, and with hydrochloric acid, which may be obtained as crystalline compounds. Thus, the compound $AuCl_3HCl,3H_2O$ is deposited from a strong solution of gold in aqua-regia. This substance is sometimes termed *chloro-auric acid*, and the double compounds with metallic chlorides, such as $AuCl_3,NaCl,2H_2O$ and $(AuCl_3,KCl)_2H_2O$, are known as *chloro-aurates*.

Auric Oxide, Au_2O_3, is obtained as a brown powder when the hydrated oxide, $Au_2O_3,3H_2O$ (or $Au(HO)_3$), is gently warmed. At 100° it begins to decompose, and at higher temperatures is completely converted into oxygen and metallic gold.

Auric oxide is feebly basic, forming a few unstable salts, in which gold replaces the hydrogen in acids. It is also a feeble acid-forming oxide, and forms salts called *aurates*, such as potassium aurate, $KAuO_2,3H_2O$, which may be regarded as being derived from an acid of the composition $HAuO_2$.

Auric oxide forms a compound with ammonia, known as *fulminating gold*, the exact composition of which is not known. It explodes with violence when dry if struck or gently warmed.

Gold Sulphides.—Two sulphides of gold have been obtained, aurous sulphide, Au_2S, and auro-auric sulphide, Au_2S,Au_2S_3 (or AuS). The latter is formed when sulphuretted hydrogen is passed into a cold solution of auric chloride—

$$8AuCl_3+9H_2S+4H_2O=2(Au_2S,Au_2S_3)+24HCl+H_2SO_4.$$

CHAPTER VI ✓

ELEMENTS OF GROUP II. (FAMILY A.)

	Atomic Weights.		Atomic Weights.
Beryllium, Be	9.1	Strontium, Sr	87.6
Magnesium, Mg	24.36	Barium, Ba	137.4
Calcium, Ca	40.1		

WITH the exception of the rare element beryllium, these metals were first obtained (although not in the pure state) by Davy, who, soon after his discovery of the metals potassium and sodium, showed that the so-called *earths* were not elementary bodies as had been supposed, but were compounds of different metals with oxygen.

The element beryllium is of later discovery, for although as early as 1798 it had been shown by Vanquelin that the particular "earth" in the mineral *beryl* was different from any other known earth, it was not until 1827 that the metal it contained was isolated by Wöhler. In a state approaching to purity, beryllium was first prepared by Humpidge, 1885.

None of the elements of this family occurs in nature in the uncombined condition; and, with the exception of magnesium and calcium, the metals themselves, in their isolated condition, are at present little more than chemical curiosities. In the case of beryllium this is due to the comparative rarity of its compounds; but with strontium, and barium, whose compounds are extremely abundant, it is owing partly to the difficulty of isolating the metals in a pure state, and also to the fact that hitherto they have received no useful application. Beryllium and magnesium are white metals, which retain their lustre in the air. Calcium, strontium, and barium on exposure to air quickly become converted into oxide.

The metals calcium and strontium, as obtained by earlier experimenters, presented a pale yellow colour (it is doubtful whether the metal barium was actually obtained by these chemists). But the calcium which has recently been obtained in considerable masses is found to be a silver-white metal.

All these metals form an oxide of the type RO. Beryllium oxide is insoluble in water; magnesium oxide is very slightly soluble (1 part in 55,000 or 100,000 parts of water), but the solution shows a feeble alkaline reaction. The calcium, strontium, and barium oxides show increasing solubility, and stronger alkalinity and causticity. On this account these elements are known as the *metals of the alkaline earths*. These three elements also form peroxides of the type RO_2.

All the monoxides are basic, and combine with acids to form salts of the types RCl_2, RSO_4, $R(NO_3)_2$.

The element beryllium (the typical element) stands apart from the others of this family in many of its chemical relations. Thus the oxide BeO, unlike the corresponding compounds of the other elements, does not combine with water to form the hydroxide. The hydroxide $Be(HO)_2$ is soluble in sodium and potassium hydroxide. In this respect beryllium exhibits its resemblance to zinc. The chloride also differs from the other chlorides in being volatile.

In its permanence in air, its colour, its high melting-point, the solubility of its sulphate, and the readiness with which its hydroxide is converted by heat into the oxide, beryllium exhibits a close similarity to magnesium. In the solubility of its hydroxide in potassium hydroxide, and in its inability to decompose water, beryllium also shows a marked resemblance to zinc.

The three elements, calcium, strontium, and barium, exhibit a closer resemblance to each other in most of their physical and chemical relations, than to either magnesium or beryllium.

They are readily distinguished by their different spectra. Barium salts, when heated in a non-luminous flame, impart to it a green colour. Calcium and strontium, under the same circumstances, each give a red colour; but the red imparted by strontium compounds is more brilliant, and less orange, than that of calcium salts. When the flames are examined by the spectroscope, the most characteristic lines given by barium are two in the bright green (Baα and Baβ). These are accompanied by a number of less brilliant lines. The spectrum of strontium consists of four specially prominent lines, one in the bright blue (Srδ), one in the orange (Srα), and two in the red (Srβ and Srγ), with others less pronounced; while that of calcium contains one brilliant green line (Caβ) and one equally brilliant orange line (Caα), besides a large number of less prominent lines.

BERYLLIUM (*Glucinum*).

Symbol Be. Atomic weight=9.1.

Occurrence.—This element occurs principally in the mineral *beryl*, a double silicate of the composition $3BeO,Al_2O_3,6SiO_2$. The transparent varieties are used as gems, the transparent green beryl being the precious *emerald*.

Phenacite is beryllium silicate Be_2SiO_4, while *chrysoberyl* has the composition BeO,Al_2O_3.

Formation.—The element is obtained by heating sodium in the vapour of beryllium chloride, all air having been previously replaced by hydrogen. The product is afterwards melted beneath fused sodium chloride, when it is obtained as a coherent solid metal. It may also be obtained by the electrolysis of the fused mixed chlorides of beryllium and potassium.

Properties.—Beryllium is a white metal resembling magnesium. It has a specific gravity of 2.1, and is moderately malleable. It does not readily tarnish in the air at ordinary temperatures, but when strongly heated, becomes coated with a protecting film of oxide. The powdered metal, when heated, takes fire, and burns with a bright light. It has no action upon water, even at the boiling temperature.

Beryllium is easily dissolved by dilute hydrochloric acid, with evolution of hydrogen. Cold dilute sulphuric acid is without action, but when heated slowly dissolves it. Nitric acid slowly attacks it when concentrated and hot. It readily dissolves in potassium hydroxide, with evolution of hydrogen.

Beryllium Compounds.—The best known are the oxide (*berylla*), BeO, a white infusible powder, insoluble in water, soluble in acids; the chloride, $BeCl_2$, obtained by heating the oxide with charcoal in a stream of chlorine, a white crystalline solid, readily fused and volatilised.

Beryllium compounds do not impart any colour to a Bunsen flame. They are characterised by possessing a sweet taste, hence the name of *glucinum* originally given to this element.

MAGNESIUM.

Symbol, Mg, Atomic weight=24.36.

Occurrence.—Magnesium is not found in the uncombined state. In combination it is widely distributed, and is extremely abundant. In the mineral *dolomite*, associated with calcium as carbonate, it occurs in mountainous masses.

Magnesite, $MgCO_3$; *kieserite*, $MgSO_4,H_2O$; *carnallite*, $MgCl_2$,

$KCl,6H_2O$, are amongst the commoner naturally occurring magnesium compounds. It is also a constituent of *asbestos*, *meerschaum*, *serpentine*, *talc*, and a large number of other silicates. As sulphate and chloride it is met with in sea-water and many saline springs.

Modes of Formation.—Magnesium was obtained by Bunsen by the electrolysis of fused magnesium chloride; and later by Matthiessen by electrolysing the fused double chloride of magnesium and potassium (carnallite).

On a manufacturing scale it was later produced by the reduction of magnesium chloride by means of sodium. A mixture of anhydrous magnesium chloride (or fused mixed chlorides of magnesium and sodium, or potassium), powdered cryolite, and sodium is thrown into a red-hot crucible, which is quickly closed. A violent reaction takes place, at the conclusion of which the melted mixture is stirred with an iron rod to cause the globules of magnesium to run together.

The crude metal is afterwards purified by distillation.

At the present time magnesium is manufactured by a process which is practically that formerly employed by Matthiessen on a small scale, but modified in detail to suit modern electrical resources. An iron crucible or melting pot is used, which is made the cathode, and the double magnesium potassium chloride (carnallite) is maintained at a temperature about 700°—*i.e.* a dull red heat—by means of gaseous fuel. The anode consists of a stout carbon rod which dips into the molten material, and is surrounded by a porcelain cylinder which conveys away the chlorine.

Properties.—Magnesium is a silvery-white metal, which does not tarnish in dry air, but becomes coated with a film of oxide when exposed to air and moisture. At a red heat it melts, and at higher temperatures may be distilled. When heated in the air it takes fire, and burns with a dazzling white light, which is extremely rich in the chemically active rays. The flash of light, obtained by projecting a small quantity of magnesium filings into a spirit flame, is used for photographic purposes. Magnesium is only moderately malleable, and is only ductile at high temperatures; it is readily pressed into the form of wire at a temperature slightly below its melting-point. Magnesium only slightly decomposes water even at the boiling-point; but when strongly heated in a current of steam, the metal takes fire (p. 173). Magnesium is rapidly dissolved by dilute acids, with brisk evolution of hydrogen, but solutions of caustic alkalies are unacted upon by it (compare Zinc). When heated with aqueous solutions of ammonium salts, hydrogen is evolved, and a double salt of magnesium and ammonium is found in the solution.

Magnesium combines directly with nitrogen, when strongly heated in that gas, forming magnesium nitride, N_2Mg_3 (p. 232).

On account of the brilliant light emitted by burning magnesium, it is employed for signalling purposes, and also in pyrotechny.

Magnesium Oxide (*magnesia*), MgO, is found native as the mineral *periclase*. It is formed when magnesium burns in the air, or when magnesium carbonate is submitted to prolonged gentle calcination, when it is obtained as a white bulky powder, known in commerce as *calcined magnesia* or *magnesia usta*.

Magnesia is extensively manufactured from the magnesium chloride occurring in the Stassfurt deposits, by first converting the chloride into carbonate and subjecting this to calcination. Magnesia has been obtained in the crystalline form, identical with that of periclase, by heating the amorphous compound in a stream of gaseous hydrochloric acid. It may be fused in the oxyhydrogen flame, and on cooling it solidifies to a vitreous mass which is sufficiently hard to cut glass. On account of its extreme refractoriness, magnesia is used for a variety of metallurgical purposes, such as the manufacture of crucibles, cupels, &c.

Magnesium Hydroxide, $Mg(HO)_2$, is found in nature as the mineral *brucite*. It is prepared by precipitating a magnesium salt by sodium or potassium hydroxide. At a dull red heat it loses water, and is converted into the oxide, and the magnesia so obtained has the property of rehydrating itself in contact with water, with evolution of heat.

Magnesium hydroxide slowly absorbs carbon dioxide, forming the carbonate ; owing to this fact, and to the property it possesses of rehydration, magnesia that has been prepared by calcination at a low temperature can be employed as a cement. Thus, if calcined magnesite be made into a paste with water, the mixture is found to harden in about twelve hours, and ultimately to acquire a hardness equal to that of Portland cement.

Magnesium Chloride, $MgCl_2$.—This salt is formed when magnesia, or magnesium carbonate, or the metal itself, is dissolved in hydrochloric acid. From this solution monosymmetric crystals of the composition $MgCl_2,6H_2O$ are deposited. When this salt is heated it loses water, and at the same time is partially decomposed into hydrochloric acid and magnesia ; in order, therefore, to prepare the pure anhydrous compound, the double magnesium ammonium chloride is first formed, by adding ammonium chloride to a solution of magnesium chloride. On evaporation, the double salt separates out, $MgCl_2,NH_4Cl,6H_2O$. This salt allows itself to be dehydrated by heating, without any decomposition of the magnesium chloride. When the dried salt is more strongly heated, ammonium chloride volatilises and leaves the anhydrous magnesium chloride as a fused mass, which congeals to a white crystalline solid. Magnesium chloride is deliquescent, and dissolves in water with evolution of heat. With alkaline chlorides it forms double salts, as the ammonium salt above mentioned. The potassium salt, $MgCl_2,KCl,6H_2O$, occurs in large quantities as the mineral *carnallite;* and the calcium salt, $2MgCl_2,CaCl_2,12H_2O$, as *tachydrite*, in the Stassfurt deposits. When a strong solution of magnesium chloride is made into a thick paste with calcined magnesia, the mass quickly sets and hardens, like plaster of Paris, and is found to contain an oxychloride having the composition $MgCl_2,5MgO$, associated with varying quantities of water. The white deposit which forms in bottles containing the solution known as *magnesia mixture* consists of $MgCl_2,5MgO,13H_2O$.

When magnesium oxychloride is heated to redness in a current of air, the magnesium is converted into oxide, and a mixture of chlorine and hydrochloric acid is evolved. The reaction may be represented as taking place as follows—

$$2MgCl_2+H_2O+O=2MgO+2HCl+Cl_2.$$

The Weldon-Péchiney process for manufacturing chlorine is based upon this reaction.

Magnesium Sulphate, $MgSO_4,7H_2O$ (*Epsom salts*), is met with in many mineral springs, and in large quantities as the mineral *kieserite*, $MgSO_4.H_2O$.

Magnesium sulphate may be obtained by decomposing *dolomite*, $(CaMg)CO_3$, with sulphuric acid, the nearly insoluble calcium sulphate being readily removed from the soluble magnesium salt. Magnesium sulphate is now very largely manufactured from *kieserite*, which in contact with water is converted from the slightly soluble monohydrated salt into $MgSO_4,7H_2O$, which is readily soluble, and is purified by recrystallisation. As usually obtained, crystallised magnesium sulphate, $MgSO_4,7H_2O$, forms colourless rhombic prisms; but when deposited from a cold supersaturated solution, it sometimes forms prisms belonging to the monosymmetric (monoclinic) system, having the same degree of hydration. Above 50°, monosymmetric prisms of the composition $MgSO_4,6H_2O$ are deposited.

When the ordinary salt, $MgSO_4,7H_2O$, is placed over sulphuric acid, it loses two molecules of water: when heated to 150° it loses six molecules, and at 200° it becomes anhydrous. At the ordinary temperature, 100 parts of water dissolve 126 parts of crystallised magnesium sulphate; the solution has a bitter taste, and acts as a purgative. With alkaline sulphates, magnesium sulphate forms a series of double salts, having the general formula $MgSO_4,R_2SO_4,6H_2O$. They are ismorphous with each other, crystallising in monosymmetric prisms. The potassium salt occurs in the Stassfurt deposits as *schönite.*

When anhydrous magnesium sulphate is dissolved in hot sulphuric acid, two acid sulphates are obtained. One, having the composition $MgSO_4H_2SO_4$, is deposited from the hot solution; while from the cold liquid the salt that crystallises has the composition $MgSO_4,3H_2SO_4$. They are at once decomposed by water.

Magnesium Carbonate, $MgCO_3$, occurs as the mineral *magnesite,* which is sometimes found as rhombohedral crystals, isomorphous with crystals of *calcite* ($CaCO_3$). Magnesium exhibits a great tendency to form basic and hydrated carbonates; the normal carbonate, $MgCO_3$, is therefore not obtained by precipitating a magnesium salt with an alkaline carbonate; the white precipitate formed under these circumstances is a basic carbonate, whose composition varies with the conditions of precipitation. If, however, this precipitate be suspended in water, and the liquid saturated with carbon dioxide, the compound dissolves (more readily under increased pressure), and when the solution is heated to 300° under pressure, in such a manner that the evolved carbon dioxide can escape, the normal anhydrous carbonate is deposited in rhombohedral crystals isomorphous with calcite. If the solution be evaporated to dryness, the normal carbonate is deposited in rhombic crystals isomorphous with *arragonite* ($CaCO_3$). Magnesium and calcium carbonates are therefore isodimorphous.

Basic Carbonates.—The mineral *hydromagnesite* is a basic carbonate of the composition $3MgCO_3,Mg(HO)_2,3H_2O$. A number of basic carbonates are formed by the precipitation of a magnesium salt with sodium carbonate. Thus, under ordinary conditions a white bulky precipitate is obtained, known in pharmacy as *magnesia* *alba levis.* Its composition, although liable to vary through the presence of other basic carbonates, is in the main the same as that of hydromagnesite.

If the precipitation be made with boiling solutions, and the precipitate so obtained be dried at 100°, a denser carbonate is obtained, termed *magnesia alba ponderosa*, $4MgCO_3,Mg(HO)_2,4H_2O$.

When an excess of sodium carbonate is employed, and the mixture is subjected to prolonged boiling, a carbonate is obtained having the composition $2MgCO_3,Mg(HO)_2,2H_2O$.

CALCIUM.

Symbol, Ca. Atomic weight=40.1.

Occurrence.—Calcium is only met with in nature in combination. It occurs in enormous quantities as the carbonate in a great variety of different minerals, such as *marble*, *limestone*, *calcspar*, and also as *coral;* and with carbonate of magnesium as *dolomite*, or *magnesian limestone.* In the form of sulphate, calcium occurs as *gypsum* and *selenite*, $CaSO_4,2H_2O$, and as *anhydrite*, $CaSO_4$. The fluoride CaF_2 occurs as *fluorspar*, and the various silicious rocks contain compound silicates of calcium and other metals. The carbonate and sulphate are present in most spring and river waters. Calcium compounds are also present in all vegetable and animal organisms. Thus, bones consist largely of calcium phosphate.

Modes of Formation.—Although calcium compounds are so extremely abundant, the metal itself, until quite recently, was scarcely more than a chemical curiosity. The element was first isolated in an impure state by Davy (1808).

More recently Moissan obtained the metal in the form of crystals by heating together sodium and calcium iodide—

$$CaI_2+2Na=2NaI+Ca.$$

The calcium dissolves in the excess of sodium, and on cooling it crystallises out. The sodium is removed by solution in absolute alcohol.

At the present time calcium is obtained commercially by the electrolysis of the fused chloride, the success of the process depending upon the device adopted for removing the metal, as it is reduced, from the action of the fused electrolyte. The cathode employed is a rod of iron which is brought just to the surface of the melted chloride. As soon as a small quantity of the metal calcium collects beneath the end of the cathode, the latter is very slowly raised by a suitable mechanical arrangement, so that the calcium may solidify upon the end of the iron rod without any interruption of the electrolysis. As this process of continuously raising the cathode proceeds, a rugged rod or bar of calcium weighing several pounds may be gradually built up.

Properties.—Calcium is a silver-white metal having a specific gravity 1.85, and melting about 760° C. It is moderately soft and malleable. In moist air it is soon converted into the hydroxide, but in dry air it remains untarnished for a considerable time. It decomposes water at the ordinary temperature, with rapid evolution of hydrogen. When heated in the air it takes fire and burns.

Oxides of Calcium.—Two oxides are known, namely, calcium monoxide, CaO, and calcium dioxide, CaO_2.

Calcium Oxide (*lime*, *quicklime*), CaO, is obtained by heating calcium carbonate to redness—

$$CaCO_3 = CO_2 + CaO.$$

On a large scale lime is manufactured by burning limestone or chalk in kilns with coal. If much clay be present with the limestone, care is required to prevent the mass from fusing when it is said to be *dead burnt*. Lime is a white amorphous substance, which is infusible by the oxyhydrogen flame, but which, when so heated, emits a bright light, known as the oxyhydrogen limelight. It absorbs moisture and carbon dioxide from the air. On account of its power of absorbing moisture, lime is frequently employed as a dehydrating agent. Thus, gases which cannot be dried by means of sulphuric acid (*e.g.* ammonia) may be deprived of moisture by being passed over calcium oxide. It is also used for withdrawing water from alcohol in the preparation of absolute alcohol. When a small quantity of water is poured upon lime the mass rapidly becomes hot, and volumes of steam are given off, the lime at the same time swelling up and crumbling to a soft, dry powder. This process is known as the *slaking* of lime, and the product is termed *slaked lime*, in contradistinction to *quick lime*. The lime enters into chemical union with water, forming calcium hydroxide, thus—

$$CaO + H_2O = Ca(HO)_2.$$

Calcium Hydroxide, $Ca(HO)_2$, is a white amorphous powder, sparingly soluble in water, and, unlike the majority of solids, it is less soluble in hot than in cold water. 100 parts of water at the ordinary temperature dissolve 0.14 part of calcium hydroxide, while at 100° the same volume of water dissolves about half that amount. This solution, known as *lime-water*, has an alkaline reaction, and absorbs carbon dioxide, with the precipitation of calcium carbonate.

Milk of Lime is the name given to a mixture of lime with less water than will dissolve it, whereby an emulsion of lime is obtained. When a thick paste of lime and water is exposed to the atmosphere, in a few days it sets, and continues gradually to harden. On this account lime is used for mortars and cements. Mortar consists of a mixture of lime and sand with water. The sand serves the double purpose of preventing shrinkage on drying, and also of rendering the mass more permeable to atmospheric carbon dioxide. The setting of mortar is due to the combined action of evaporation and absorption of carbon dioxide.

Calcium Dioxide, CaO_2, is obtained by adding lime-water to hydrogen peroxide, or to sodium peroxide acidulated with dilute nitric acid; sparingly soluble crystals of $CaO_2,8H_2O$ separate out, which at 130° lose their water. When more strongly heated the monoxide is formed with evolution of oxygen.

Calcium Chloride, $CaCl_2$, occurs in sea and river waters, and is present in *tachydrite* of the Stassfurt deposits. It is obtained in large quantities as a bye-product in many manufacturing processes, such as that of potassium chlorate, ammonia from ammonium chloride, &c. It may be obtained by the action of hydrochloric acid upon calcium carbonate, and is deposited on concentration, in large colourless, deliquescent, hexagonal prisms, $CaCl_2,6H_2O$, which melt at 29° in their water of crystallisation. When heated below 200° the crystals part with four molecules of water, and above 200° become anhydrous. As thus obtained the anhydrous salt is a porous mass, which is extremely hygroscopic, and on this account is used as a desiccating agent, both for gases and liquids. At a red heat it fuses, and on cooling solidifies to a crystalline, deliquescent mass. Calcium chloride combines with ammonia, forming the compound $CaCl_2,8NH_3$. Calcium chloride, therefore, cannot be employed for drying gaseous ammonia.

Crystallised calcium chloride is extremely soluble in water; 100 parts of water at 16° dissolve 400 parts of the salt, the solution being attended with considerable absorption of heat. When mixed with powdered ice or snow liquefaction of both the solids rapidly takes place, and the consequent absorption of heat lowers the temperature of the mixture to $-40°$.

Bleaching-Powder (*chloride of lime*), Ca(OCl)Cl.—This important compound is manufactured on a large scale by the action of chlorine upon slaked lime. The hydrated lime is spread upon the floor of the bleaching-powder chambers to a depth of three or four inches, and raked into ridges or furrows with a special wooden rake. Chlorine is then led into the chambers, which are provided with glass windows to enable the operator to examine the colour of the atmosphere within. At first the absorption of the chlorine is rapid, but as the reaction proceeds it becomes slower, and the lime is from time to time raked over to expose a fresh surface. The lime is left in contact with the gas for twelve to twenty-four hours. The excess of chlorine is absorbed by projecting into the chamber a shower of fine lime dust by means of a mechanical fan-distributor. This, in settling, rapidly absorbs all the chlorine, and the chambers can then be opened without any unpleasant smell of chlorine being perceptible.

The reaction which takes place is expressed by the equation—

$$Ca(HO)_2+Cl_2=Ca(OCl)Cl+H_2O.$$

It was formerly believed that bleaching-powder was a mechanical mixture of calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$, but it has been conclusively shown that the substance does not contain any free calcium chloride. It may, however, be regarded as a compound consisting of equivalent proportions of these two salts, and its composition may be expressed by the formula $Ca(OCl)_2,CaCl_2$, which corresponds to 2Ca(OCl)Cl.

The relation in which bleaching-powder stands to calcium chloride on the one hand and calcium hypochlorite on the other will be seen by the following formulæ—

Calcium Chloride.	Calcium Hypochlorite.	Bleaching-Powder, or Calcium Chloro-hypochlorite.
Cl—Ca—Cl	ClO—Ca—OCl	Cl—Ca—OCl.

In practice the absorption of chlorine by the lime is never as complete as is represented by the above equation, and the commercial value of the product depends upon the amount of *available chlorine* it contains, *i.e.* chlorine which is evolved on treating the compound with hydrochloric or sulphuric acid. This ranges from 30 to 38 per cent.

When treated with water, bleaching-powder is converted into calcium chloride and hypochlorite, thus—

$$2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2.$$

Bleaching-powder decomposes slowly even in stoppered bottles, and more rapidly on exposure to atmospheric moisture and carbon dioxide.

When acted upon by acids chlorine is evolved, thus—

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2$$
$$Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

When a solution of bleaching-powder is treated with very dilute acids, hypochlorous acid is first liberated, which in contact with hydrochloric acid yields chlorine—

$$(1)\quad Ca(OCl)_2.Aq + 2HCl.Aq = CaCl_2 + 2HClO.Aq.$$
$$(2)\quad HClO + HCl = H_2O + Cl_2.$$

In the process of bleaching, the material is first steeped in a dilute solution of bleaching-powder and then in dilute acid. The hypochlorous acid first formed is decomposed in the presence of excess of hydrochloric acid, generating chlorine within the fibres of the wet cloth.

Calcium Sulphate, $CaSO_4$, occurs as the mineral *anhydrite*, and in the hydrated condition as *gypsum*, $CaSO_4,2H_2O$, of which *satinspar* (or *fibrous gypsum*), *alabaster*, and *selenite* are different varieties. It is obtained in the hydrated condition by precipitation from a solution of calcium chloride, on the addition of sulphuric acid or a soluble sulphate. When dried at 110° to 120° it loses a portion of its water, leaving the hydrate, $(CaSO_4)_2,H_2O$; at 200° it becomes anhydrous. Calcium sulphate, in the hydrated condition, is slightly soluble in water, the solubility reaching a maximum at 35°, when 1 part of the compound requires 432 parts of water for its solution ; above this temperature the solubility again diminishes. Its solubility is increased by the presence of alkaline chlorides and free hydrochloric acid.

When boiled in strong sulphuric acid calcium sulphate partially dissolves, and on cooling an acid sulphate crystallises out, having the composition $CaSO_4,H_2SO_4$.

Plaster of Paris is calcium sulphate which has been partially deprived of its water of hydration by heat, and converted into the hydrate, $(CaSO_4)_2,H_2O$. It is manufactured by burning gypsum in a kiln or oven in such a way that the carbonaceous fuel does not come in contact with the sulphate, which would result in its reduction to sulphide; the temperature is not allowed to exceed about 130°. If heated more strongly (above 200°) the sulphate becomes anhydrous, and is said to be *dead burnt;* in this condition its property of *setting* when mixed with water is greatly impaired. When plaster of Paris is made into a paste with water it rapidly sets to a hard mass; this setting is due to its rehydration, whereby gypsum is reformed, thus—

$$(CaSO_4)_2,H_2O + 3H_2O = 2CaSO_4,2H_2O.$$

Calcium Carbonate, $CaCO_3$.—This compound is extensively met with in nature, as *limestone*, *chalk*, *marble*, and innumerable varieties of *calcspar.* It is formed when lime is exposed to atmospheric carbon dioxide. It is obtained when an alkaline carbonate is added to a soluble calcium salt.

Calcium carbonate is dimorphous; it occurs as *arragonite* in crystals belonging to the orthorhombic system, and as calcspar in crystals belonging to the hexagonal system. Both these crystalline varieties can be artificially obtained; when deposited from solutions at the ordinary temperature the crystals are identical with calcite; but when crystallised from hot solutions, they form rhombic crystals corresponding to arragonite.

Calcium carbonate is nearly insoluble in water; 1000 grammes of water dissolve .0018 gramme of the compound. It is more soluble in water charged with carbon dioxide, forming the acid carbonate of lime, $CaCO_3,H_2CO_3$, or $H_2Ca(CO_3)_2$.

1000 grammes of water saturated with carbon dioxide will dissolve, at 0°, 0.7 gramme of calcium carbonate. By increasing the pressure (thereby increasing the amount of dissolved gas) as much as 3 grammes of calcium carbonate may be dissolved. When this solution is boiled the acid carbonate is decomposed (page 221).

Calcium Phosphate (*tricalcium orthophosphate*), $Ca_3(PO_4)_2$, is the most important of the phosphates of calcium. It is found as the mineral *osteolite*, $Ca_3(PO_4)_2,2H_2O$, and also as *sombrerite*, *estramadurite*, and *coprolites.* *Apatite* consists of phosphate and fluoride, $3Ca_3(PO_4)_2,CaF_2$; and the mineral constituents of bones consist chiefly of calcium phosphate.

It is obtained in a pure state by the addition of ordinary sodium phosphate to a solution of calcium chloride in the presence of ammonia. The precipitate is decomposed on boiling into an insoluble basic salt and a soluble acid salt. Although nearly insoluble in pure water, calcium phosphate dissolves in water containing salts in solution, such as sodium chloride or nitrate, or even dissolved carbon dioxide. On this fact depends the readiness with which this substance is absorbed by the roots of plants.

Calcium phosphate is readily soluble in both nitric and hydrochloric acids. It is decomposed by sulphuric acid, with the formation of monocalcium orthophosphate and calcium sulphate, thus—

$$Ca_3(PO_4)_2+2HS_2O_4=2CaSO_4+H_4Ca(PO_4)_2.$$

This mixture of calcium sulphate and monocalcium phosphate is known as *superphosphate of lime*, and is largely used as an artificial manure.

With a larger quantity of sulphuric acid the phosphate is converted into tribasic phosphoric acid. (See Phosphorus, page 453.)

Calcium Carbide, CaC_2.—This compound is produced when lime or chalk is heated with carbon in the electric furnace. It is also obtained as a second product in the manufacture of phosphorus when calcium phosphate is heated with carbon (see Phosphorus). Calcium carbide is manufactured on an extensive scale for use in the preparation of acetylene (page 318).

Calcium Sulphide, CaS, is formed when sulphuretted hydrogen is passed over heated lime—

$$Ca(HO)_2+H_2S=CaS+2H_2O.$$

Or by heating calcium sulphate with carbon—

$$CaSO_4+4C=CaS+4CO.$$

Calcium sulphide is decomposed on boiling with water, forming calcium hydroxide and hydrosulphide, thus—

$$2CaS+2H_2O=Ca(HO)_2+Ca(HS)_2.$$

Calcium sulphide (in common with barium and strontium sulphides), *as usually obtained*, possesses the property of emitting a feeble light (or phosphorescence) in the dark, after being previously exposed to a bright light. The light emitted gradually diminishes in intensity, but on re-exposing the compound to the light its luminosity is again restored. This property has been long known, and calcium sulphide was formerly termed *Canton's phosphorus.* The material formerly known as *Bononian* (or *Bolognian*) *phosphorus* is the corresponding barium compound.

These various sulphides are now manufactured for the preparation of so-called luminous paint. The phosphorescence of these compounds appears to be due to the presence of small quantities of foreign substances; thus, not only is the particular colour of the light emitted changed by the intentional introduction of minute traces of bismuth, cadmium, manganese, zinc, and many other metals, but it has been shown, in the case of calcium sulphide, that the perfectly pure substance does not exhibit phosphorescence.

STRONTIUM.

Formula, Sr. Atomic weight=87.6.

Occurrence.—The chief natural compounds of this element are *strontianite*, $SrCO_3$, and *celestine*, $SrSO_4$.

Modes of Formation.—The metal was first obtained in small quantity by Davy, by the electrolysis of the hydroxide, or chloride, moistened with water.

It is more advantageously obtained by electrolysing the fused chloride. An amalgam of mercury and strontium (from which the strontium may be separated by volatilising the mercury in a stream of hydrogen) has been obtained by heating a saturated solution of strontium chloride with sodium amalgam.

Properties.—Strontium, as obtained by these methods, possesses a pale yellow colour. It is readily oxidised by air, and decomposes water at ordinary temperatures; when heated in the air it burns brilliantly.

Oxides of Strontium.—Two oxides, corresponding to those of calcium, are known, namely, strontium monoxide, SrO, and dioxide, SrO_2.

Strontium Monoxide (*strontia*), SrO, is obtained by heating the nitrate or carbonate. It is prepared on a large scale by decomposing strontium carbonate by superheated steam; carbon dioxide is evolved, and strontium hydroxide remains, which on ignition forms the monoxide. Strontia strongly resembles lime. When treated with water it slakes with evolution of heat, forming strontium hydroxide, $Sr(HO)_2$. The hydroxide is more soluble in water than the lime compound, and the solution on cooling deposits tetragonal crystals, $Sr(HO)_2,8H_2O$. The solution is strongly alkaline.

Strontium hydroxide combines with sugar, forming a saccharate of strontia, which is readily decomposed by carbon dioxide. On this account it is prepared on a large scale for use in the manufacture of beet-sugar. One process by which it is obtained on a commercial scale consists in first forming strontium sulphide, by reducing the natural sulphate with carbon, and treating the solution of the sulphide with sodium hydroxide, thus—

$$SrS + NaHO + H_2O = Sr(HO)_2 + NaHS.$$

Strontium Dioxide, SrO_2.—When hydrogen peroxide is added to a solution of strontium hydroxide, a hydrate of the peroxide separates out in the form of pearly crystals, $SrO_2,8H_2O$. On gently heating this compound, it is converted into the anhydrous peroxide. On heating to redness it evolves oxygen, and is converted into the monoxide.

Strontium Chloride, $SrCl_2$, is obtained from strontianite by the action of hydrochloric acid. The salt deposits from the solution in deliquescent hexagonal prisms, $SrCl_2,6H_2O$, isomorphous with the corresponding calcium compound.

Strontium Sulphate, $SrSO_4$.—The native compound *celestine* occurs in amorphous fibrous masses, and also in rhombic crystals. The name of the mineral is derived from the fact that it usually has a light blue colour. It is produced by precipitation from a strontium salt by sulphuric acid. It is only slightly soluble in cold water, and still less in hot. When boiled with solutions of alkaline carbonates, strontium sulphate is completely converted into strontium carbonate—

$$SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4.$$

In this respect strontium sulphate differs from barium sulphate, which under these conditions remains unchanged. On treatment with strong sulphuric acid, strontium sulphate forms $SrSO_4,H_2SO_4$, which, like the corresponding calcium compound, is converted by water into sulphuric acid and the normal sulphate.

Strontium Nitrate, $Sr(NO_3)_2$, is obtained by dissolving the natural carbonate in dilute nitric acid. On concentration, the anhydrous salt separates out in octahedrons. From dilute solution, on cooling, it forms monosymmetric prisms, $Sr(NO_3)_2,4H_2O$, which effloresce on exposure to the air. When heated with carbon, or other readily combustible substances, the mixture inflames and burns with the red colour characteristic of strontium compounds; strontium nitrate is therefore largely used in pyrotechny for the production of red fire. This property is most readily illustrated by mixing dry powdered strontium nitrate with ammonium picrate, and igniting the mixture, which burns with a brilliant red light.

BARIUM.

Symbol, Ba. Atomic weight=137.4.

Occurrence.—The most abundant natural compounds of barium are *heavy spar*, $BaSO_4$, and *witherite*, $BaCO_3$. It occurs also, associated with calcium, in the mineral *barytocalcite*, $BaCO_3,CaCO_3$.

Modes of Formation.—The element barium is more difficult to isolate than either strontium or calcium, and it is doubtful whether pure barium has ever been obtained. Davy electrolysed various barium salts, made into a thick paste with water, using mercury as the negative electrode: in this way an amalgam of barium was formed, from which, on distilling away the mercury, a dark porous mass was obtained. Amalgams of barium and mercury have been prepared in other ways, but it has been shown that the product obtained after distilling the mercury from these is not pure barium, but is a solid alloy or compound of barium with mercury.

By the electrolysis of the fused chloride, Matthiessen obtained small globules of metal, which on exposure to the air rapidly oxidised. More recent experimenters fail to obtain the metal by this process (Limb., *Compt. Rend.*, 112).

Oxides of Barium.—Two oxides are known, namely, barium monoxide, BaO, and dioxide, BaO_2.

Barium Monoxide (*baryta*), BaO, is usually prepared by heating the nitrate. The mass fuses and evolves oxygen and oxides of nitrogen, leaving a greyish white friable residue of the oxide. It may also be obtained by heating the carbonate; but as the temperature necessary to expel the carbon dioxide is very high, it is usual to mix the carbonate with lampblack, tar, or other substances which on heating will yield carbon, when the conversion takes place more readily, carbon monoxide being evolved, thus—

$$BaCO_3 + C = BaO + 2CO.$$

Small quantities may readily be obtained by heating barium iodate in a porcelain crucible, when the iodate is decomposed as follows—

$$Ba(IO_3)_2 = BaO + I_2 + 5O.$$

Barium oxide is a strongly caustic and alkaline compound; in contact with water it slakes with evolution of so much heat that the mass may become visibly red hot if too much water be not added.

When heated to a dull red heat in oxygen, or air, it takes up an additional atom of oxygen and forms the dioxide (see p. 184).

Barium Hydroxide, $Ba(HO)_2$, is obtained when the monoxide is slaked with water. It is manufactured by first heating the powdered native sulphate with coal, when a crude barium sulphide is formed. This is then heated in a stream of moist carbon dioxide, whereby it is converted into the carbonate, and superheated steam is then passed over the heated carbonate—

$$BaS + H_2O + CO_2 = BaCO_3 + H_2S.$$
$$BaCO_3 + H_2O = Ba(HO)_2 + CO_2.$$

Barium hydroxide is soluble in water: the solution, known as *baryta-water*, absorbs carbon dioxide, with the precipitation of barium carbonate.

The aqueous solution deposits crystals of hydrated barium hydroxide, $Ba(HO)_2,8H_2O$, in the form of colourless tetragonal prisms, which on exposure to the air lose seven molecules of water.

Barium hydroxide, when heated in a current of air, yields barium dioxide.

Barium hydroxide was formerly employed in sugar-refining, but owing to its poisonous nature it has been superseded by strontium hydroxide (*q.v.*).

Barium Dioxide (*barium peroxide*), BaO_2.—This oxide is obtained by heating the monoxide to a low red heat in a stream of oxygen, or of air which has been deprived of atmospheric carbon dioxide.

The pure compound may be obtained by adding an excess of baryta-water to hydrogen peroxide, when hydrated barium peroxide separates out in crystalline scales—

$$Ba(HO)_2 + H_2O_2 + 6H_2O = BaO_2,8H_2O.$$

On drying in vacuo at 130° this compound loses water and is converted into the anhydrous peroxide.

The commercial peroxide may be purified by treatment with dilute hydrochloric acid, whereby barium chloride and hydrogen peroxide are formed. After the removal of insoluble impurities by filtration, baryta-water is cautiously added, which causes the precipitation of ferric oxide and silica. The liquid is then filtered, and to the clear liquid, consisting of a solution of barium chloride and hydrogen peroxide, an excess of strong baryta-water is added, when the hydrated barium peroxide is precipitated, as already explained.

Barium peroxide is a grey powder, which on being heated to a bright red heat gives up oxygen and forms the monoxide (p. 184).

Dilute acids decompose barium peroxide, with formation of hydrogen peroxide and a barium salt. Concentrated sulphuric acid forms barium sulphate and ozonised oxygen. When gently warmed in a stream of sulphur dioxide, the mass becomes incandescent and forms barium sulphate—

$$BaO_2 + SO_2 = BaSO_4.$$

Barium Chloride, $BaCl_2$, may be obtained by dissolving the natural carbonate in hydrochloric acid. It may be obtained from the natural sulphate, either by first converting it into the sulphide, and decomposing that with hydrochloric acid, or by roasting the mineral with powdered coal, limestone, and calcium chloride, when the following reactions take place—

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + CaCl_2 = BaCl_2 + CaS.$$

The barium chloride is dissolved in water, and an insoluble oxysulphide of calcium remains.

Barium chloride forms colourless rhombic tables, $BaCl_2,2H_2O$, which at 15.6° are soluble to the extent of 43.5 parts in 100 parts of water. The salt is nearly insoluble in hydrochloric acid, and may therefore be precipitated from an aqueous solution by the addition of this acid.

Barium chloride, in common with all the soluble salts of this element, is highly poisonous.

Barium Sulphate, $BaSO_4$, is the most abundant naturally occurring barium compound. It is frequently met with as large rhombic crystals. The specific gravity of the mineral is 4.3 to 4.7; and on account of its high specific gravity it received the name of *barytes*, or *heavy spar*.

It is formed as a heavy white precipitate when sulphuric acid, or a soluble sulphate, is added to a solution of a barium salt. It is insoluble in water and only very slightly soluble in dilute acids.

It is soluble in hot concentrated sulphuric acid, especially when freshly precipitated ; and the solution deposits, on cooling, an acid sulphate, $BaSO_4,H_2SO_4$. On exposure to moisture the solution deposits crystals of $BaSO_4,H_2SO_4,2H_2O$. Both of these compounds, in contact with water, yield insoluble normal barium sulphate and sulphuric acid.

Precipitated barium sulphate is largely used as a pigment, known as *permanent white.*

Barium Nitrate, $Ba(NO_3)_2$, is obtained by dissolving the native carbonate, or the sulphide, in dilute nitric acid. It is also formed by double decomposition, when hot saturated solutions of sodium nitrate and barium chloride are mixed. The salt crystallises in large colourless octahedrons. 100 parts of water at the ordinary temperature dissolve 9 parts, and at 100°, 32.2 parts of barium nitrate. When strongly heated it is converted into barium oxide, with the evolution of nitrogen peroxide, oxygen, and nitrogen.

Barium nitrate is used in pyrotechny, in the preparation of mixtures for green fire.

Barium Sulphide, BaS, is obtained by methods analogous to those for preparing calcium sulphide (page 583), which it closely resembles in its properties.

CHAPTER VII

ELEMENTS OF GROUP II. (FAMILY B.)

Zinc, Zn	65.4
Cadmium, Cd	112.4
Mercury, Hg	200

THE three elements composing this family do not exhibit such a close resemblance to each other as exists between barium, strontium, and calcium; for although zinc and cadmium are very closely related, mercury in many respects differs widely from these, and from all the other elements in the same group.

Cadmium and zinc are almost invariably found associated together in nature, they are both fairly permanent in the air, and both readily take fire and burn when strongly heated, forming the oxides. Both are acted upon by dilute hydrochloric and sulphuric acids, with evolution of hydrogen, and most of their salts are isomorphous.

Mercury is peculiar in being liquid at ordinary temperatures. Zinc and cadmium melt at 430° and 320° respectively, while mercury melts at $-38.8°$. It is quite unacted upon by oxygen at ordinary temperatures, and combines with extreme slowness when heated. Its oxide, also, is readily decomposed by heat into its elements.

Dilute hydrochloric and sulphuric acids are entirely without action upon it, and it forms no hydroxide.

Mercury also differs from zinc and cadmium in forming two elementary ions, giving rise to mercurous and mercuric salts. Both zinc and cadmium have only one ion and form only one series of salts.

The hydroxide of zinc, $Zn(HO)_2$, differs from the corresponding cadmium compound, in being soluble in alkaline hydroxides.

These three elements resemble each other, and differ from those of family A of this group, in that they can be volatilised, mercury at a temperature about 357°, cadmium and zinc at temperatures approaching 1000°.

These three elements are also alike, in that their vapours consist of mono-atomic molecules.

ZINC.

Symbol, Zn. Atomic weight=65.4.

Occurrence.—Zinc is stated to have been found in Australia in the uncombined condition; with this exception, it is always met with in combination, chiefly as carbonate in *calamine* or *zinc-spar*, $ZnCO_3$, and as sulphide in *zinc-blende*, or *black-jack*, ZnS. Other ores are *red zinc ore*, ZnO; and *franklinite*, $(ZnFe)O,Fe_2O_3$.

Gahnite, or *zinc-spinnelle*, has the composition ZnO,Al_2O_3.

Modes of Formation.—The ores chiefly employed for the preparation of zinc are the carbonate and sulphide, although in New Jersey the red oxide and franklinite are used. The process consists of two operations, namely, first, the conversion of the ore into oxide of zinc, by calcination; and, second, the reduction of the oxide by means of coal at a high temperature. The calcination of the natural carbonate is readily accomplished, this compound merely giving up its carbon dioxide at a high temperature—

$$ZnCO_3 = ZnO + CO_2.$$

In the case of zinc-blende, the operation consists in the oxidation of both the sulphur and the zinc by atmospheric oxygen, thus—

$$ZnS + 3O = ZnO + SO_2.$$

Considerable care has to be exercised in order to prevent the formation of zinc sulphate, which, in the subsequent operation, would be reconverted into sulphide, and so lost. The finely crushed calcined ore is mixed with coke or coal and heated to bright redness in earthenware retorts, when the oxide is reduced, with the formation of carbon monoxide, and the metal distils and is collected in iron receivers. Zinc ores frequently contain small quantities of cadmium, and as this metal is more readily volatilised than zinc, it passes over in the first portions of the distilled product.

The two processes now almost exclusively in use for the reduction of zinc, known as the *Silesian* and the *Belgian* process,* differ only in metallurgical details, &c.

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* The old method, known as the *English process*, or *distillation per descensum*, is entirely obsolete. For details of this and all other metallurgical processes, the student is referred to treatises on metallurgy, such as Percy.

Commercial zinc usually contains carbon, iron, and lead, and occasionally arsenic and cadmium. It may be obtained in a higher degree of purity by careful distillation, but pure zinc is best obtained by first preparing the pure carbonate by precipitation, and then calcining and finally reducing with charcoal obtained from sugar.

Properties.—Zinc is a bluish-white, highly crystalline, and brittle metal. At a temperature of 300° it can be readily powdered in a mortar, while between 100° and 150° it admits of being drawn into wire or rolled into thin sheet. The presence of a small quantity of lead greatly enhances this property, but is detrimental when the zinc is required for making brass. Zinc which has been either rolled or drawn no longer becomes brittle when cold, but retains its malleability.

Zinc melts at a temperature about 430,° and when heated in air much beyond this point the metal takes fire and burns with a bluish-white flame, the brilliancy of which becomes dazzling if a stream of oxygen be projected upon the burning mass. The product of its combustion is zinc oxide, ZnO, which forms a soft, white, flocculent substance resembling wool, and formerly known as *philosopher's wool.*

The boiling-point of zinc is about 930°.

Zinc is permanent in dry air at ordinary temperatures, but when exposed to moist air it tarnishes superficially; it is also unattacked by water at the boiling temperature. It is soluble in a hot solution of sodium or potassium hydroxide, with evolution of hydrogen (p. 175).

Pure zinc is scarcely acted upon by pure sulphuric or hydrochloric acid, either dilute or strong. The presence of small quantities of impurities, however, determines the solution of the metal with the rapid evolution of hydrogen, hence ordinary commercial zinc is readily attacked by these acids, and also decomposes water at the boiling-point, with the evolution of hydrogen.*

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* The difference between the behaviour of acids towards pure and commercial zinc was formerly explained on the ground that the impurities present formed with the zinc a voltaic couple, whereby local electric currents were set up, while in the case of pure zinc no such action took place. The recent observations of Pullinger (*Chem. Soc.*, 57) and Weeren (*Berichte*, 24) show that this is not a complete explanation. Weeren concludes that the insolubility of pure zinc in dilute acids is due to the formation of a film of condensed hydrogen upon the surface of the metal, which stops all further action. The addition of oxidising agents, such as hydrogen peroxide, or dilute sulphuric acid which has

Zinc is extensively used in the process of *galvanising* iron, which consists in coating iron with a film of zinc, not by electrical deposition, as would be implied by the name, but by dipping the iron into a bath of molten zinc. The layer of zinc preserves the iron from rusting. *Galvanised iron* is better able to withstand the action of air and moisture than tinned iron, hence it is extensively used for wire netting, corrugated roofing, water tanks, and other purposes where the metal is exposed to the oxidising influence of air and water.

Alloys of Zinc.—Zinc forms a number of useful alloys, the most important of which are the various forms of brass (see Copper). With certain metals, such as tin, copper, and antimony, zinc will mix in all proportions ; while with others, such as lead and bismuth, it is only possible to obtain solid alloys of definite composition. When, therefore, lead and zinc are melted together, although in the molten condition the mixture is homogeneous, on cooling the metals separate into two layers, the lighter zinc rising to the surface. The separation of the metals, however, is not perfect, for the zinc will have dissolved a certain quantity of the lead (1.2 per cent.), and the lower layer of lead is found to have dissolved a small proportion of zinc (1.6 per cent.), just as water and ether, when shaken together, separate into two layers, the uppermost being an ethereal solution of water, and the lower an aqueous solution of ether.

This property is made use of in the extraction of silver from lead (see p. 561).

The so-called *German silver*, or *nickel silver*, is a nearly white alloy of copper, nickel, and zinc.

Bronze coinage consists of 95 parts of copper, 4 of tin, and 1 of zinc, the small proportion of zinc giving to the alloy an increased hardness and durability.

Zinc Oxide, ZnO, the only oxide of zinc, occurs native as *red zinc ore*, the colour being due to the presence of manganese. It is

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been electrolysed, and therefore contains presulphuric acid, tends to destroy this film by oxidising the hydrogen, and therefore promotes the solution of the zinc. He also finds, that by mechanically removing this layer of hydrogen, either by constantly brushing the metallic surface or placing the materials under reduced pressure, the solution of the zinc by the acid is promoted. It is also found that the character of the surface of the metal, whether smooth or rough, affects the result ; zinc that is unacted upon when its surface is perfectly smooth is more readily attacked by the dilute acid when its surface is rough.

formed as a soft white substance when zinc is burnt in the air. It is manufactured under the name of *zinc white* by the combustion of zinc, the fumes being led into condensing-chambers, where the oxide collects.

Zinc oxide is a pure white substance, which when heated becomes yellow, but again becomes white on cooling. When strongly heated in oxygen, it may be obtained in the form of hexagonal crystals; such crystals are occasionally found in the cooler parts of zinc furnaces. The oxide does not fuse in the oxyhydrogen flame, but, like lime, under these circumstances it becomes intensely incandescent; for some time after being so heated it appears phosphorescent in the dark. It is insoluble in water, and does not combine directly with water to form the hydroxide. It dissolves in acids, giving rise to the different zinc salts. Zinc oxide is largely used in the place of "white lead" as a pigment; although it does not equal white lead in covering power, or *body*, it possesses the advantage of not being blackened by exposure to atmospheric sulphuretted hydrogen.

Zinc Hydroxide, $Zn(HO)_2$, is formed as a white flocculent precipitate, when either sodium or potassium hydroxide, or a solution of ammonia, is added to a solution of zinc sulphate. The compound is soluble in an excess of either alkali, and is deposited from a strong solution in regular octahedra of the hydrated hydroxide, $Zn(HO)_2,H_2O$. Both of these compounds on heating readily lose water, and are converted into the oxide.

Zinc Chloride, $ZnCl_2$, is formed by the direct combination of zinc with chlorine, or by the action of hydrochloric acid upon the metal. It is also obtained in the anhydrous state by distilling a mixture of mercuric chloride and zinc, or a mixture of anhydrous zinc sulphate and calcium chloride.

It is usually prepared on a large scale by dissolving zinc in hydrochloric acid, and after precipitating any manganese and iron, the liquid is boiled down in enamelled iron vessels, until on cooling it solidifies; it is usually cast into sticks.

Zinc chloride is a soft, white, easily fusible solid, which volatilises and distils without decomposition. It is extremely deliquescent, and readily soluble in water and in alcohol, its solution being powerfully caustic. From a strong aqueous solution deliquescent crystals are deposited, having the composition $ZnCl_2,H_2O$.

When the aqueous solution is evaporated, partial decomposition takes place, hydrochloric acid being evolved and basic compounds being precipitated, consisting of combinations of the chloride and oxide. Hence, during the concentration of the liquid in the preparation of zinc chloride, hydrochloric acid is added to redissolve this compound.

A paste made by moistening zinc oxide with zinc chloride rapidly sets to a hard mass; this mixture, under the name of oxychloride of zinc, is employed in dentistry as a filling or stopping for teeth.

Zinc chloride unites with alkaline chlorides, forming a series of crystalline double salts having the general formula $ZnCl_2,2RCl$.

Zinc Sulphate, $ZnSO_4$, is formed when zinc is dissolved in sulphuric acid. It is obtained on a large scale by roasting the natural sulphide, whereby it is partially converted into the sulphate, which is then extracted with water.

The salt crystallises from its aqueous solution at ordinary temperatures in colourless rhombic prisms, $ZnSO_4,7H_2O$, isomorphous with $MgSO_4,7H_2O$. It is extremely soluble in water: 100 parts of water at the ordinary temperature dissolve 160 parts, and at 100°, 653.6 parts of the crystalline salts. When exposed to the air, the crystals slowly effloresce, and if placed in vacuo over sulphuric acid, or if heated to 100°, they lose six molecules of water, leaving the monohydrated salt $ZnSO_4,H_2O$. At a temperature about 300° this is converted into the anhydrous compound, and at a white heat it gives off sulphur dioxide and oxygen, leaving the oxide.

The hydrated salt, $ZnSO_4,6H_2O$, is obtained in the form of monosymmetric crystals, when the salt is deposited at temperatures above 40°. This compound is isomorphous with $MgSO_4,6H_2O$.

Zinc sulphate combines with alkaline sulphates, forming a series of double salts, having the general formula $ZnSO_4,R_2SO_4,6H_2O$, which are also isomorphous with the corresponding magnesium compounds (page 576).

Zinc sulphate, in common with all the soluble salts of zinc, has an astringent taste, and is poisonous.

Zinc Sulphide, ZnS.—The natural compound, *zinc-blende*, is usually dark-brown or black, and exhibits crystalline forms belonging to the regular system. The mineral *wurtzite* is a less common variety of zinc sulphide, crystallising in hexagonal prisms. Zinc sulphide is obtained as a white amorphous precipitate when an alkaline sulphide is added to a solution of a zinc salt, or when sulphuretted hydrogen is passed through an alkaline solution of a zinc salt.

Precipitated zinc sulphide is insoluble in acetic acid, but readily dissolves in dilute mineral acids, with evolution of sulphuretted hydrogen ; hence the compound is not formed when sulphuretted hydrogen is passed through a solution of a zinc salt containing a free mineral acid.

Zinc Carbonate, $ZnCO_3$, is obtained as a white powder when hydrogen sodium carbonate is added to a solution of zinc sulphate.

If normal sodium carbonate be employed, the precipitated zinc compound consists of a basic carbonate, whose composition varies with the conditions of temperature and concentration of the liquids.

A basic carbonate, having the composition $ZnCO_3,2Zn(HO)_2,H_2O$, is employed as a pharmaceutical preparation under the name *zinci carbonas.*

CADMIUM.

Symbol, Cd. Atomic weight = 112.4.

Occurrence.—Cadmium is never found in the uncombined state. The only natural compound of which cadmium is the chief constituent is the extremely rare mineral *greenockite*, which is the sulphide, CdS. Cadmium occurs in small quantities in many zinc ores, such as the sulphide and carbonate ; and in the process of extracting zinc from these ores, the cadmium is obtained in the first portions of the product of the distillation, partly as metal and partly as oxide.

Mode of Formation.—The crude product of distillation is dissolved in dilute sulphuric or hydrochloric acid, and the cadmium precipitated as sulphide by means of sulphuretted hydrogen. The cadmium sulphide is then dissolved in strong hydrochloric acid, and precipitated as carbonate by means of ammonium carbonate. The washed and dried carbonate is first converted into oxide by calcination, and finally mixed with charcoal and distilled.

Properties.—Cadmium is a bluish-white metal resembling zinc in appearance, but much more malleable and ductile. It tarnishes superficially on exposure to the air, and, when strongly heated, burns with the formation of a brown smoke of cadmium oxide, CdO. The metal is attacked by dilute hydrochloric and sulphuric acids, with the evolution of hydrogen. It readily dissolves in nitric acid, yielding the nitrate, with the formation of oxides of nitrogen. Cadmium is less electro-positive than zinc, and is precipitated in the metallic condition from its solutions by that metal.

Cadmium melts at 320°, and boils about 745°. When volatilised in an atmosphere of hydrogen, it forms crystals belonging to the regular system.

Cadmium Oxide, CdO, is formed as a brown fume or smoke when cadmium burns in the air. It may be obtained by heating the carbonate or nitrate. That obtained by the ignition of the latter salt is in the form of minute crystals, having a bluish-black appearance. Cadmium oxide is insoluble in water, but dissolves in acids yielding cadmium salts. It is infusible in the oxyhydrogen flame, but is readily reduced when heated on charcoal before the blowpipe ; and the reduced metal, as it volatilises and burns, forms a characteristic brown incrustation of oxide upon the charcoal.

Cadmium Chloride, $CdCl_2$, is obtained by the action of hydrochloric acid upon the metal or the oxide. The salt is deposited from the solution in white silky crystals, having the composition $CdCl_2,2H_2O$. On exposure to the air the crystals effloresce, and when heated become anhydrous.

Cadmium Sulphide, CdS, is obtained as a bright yellow precipitate when sulphuretted hydrogen is passed through a solution of a cadmium salt. The precipitate is soluble in concentrated hydrochloric and nitric acids, and in warm dilute sulphuric acid. Cadmium sulphide is insoluble in ammonium sulphide ; this property readily distinguishes it from arsenious sulphide, which in colour it closely resembles.

Cadmium sulphide is used as a pigment, both in oil and water-colours.

MERCURY.

Symbol, Hg. Atomic weight = 200.

Occurrence.—In the uncombined state mercury is met with in small globules, disseminated through its ores, especially the sulphide. It is also occasionally found as an amalgam with silver and gold. The principal ore is *cinnabar*, HgS, and the chief mines of this ore are those of Almaden (Spain), Idria (Carniola), California, and the Bavarian Palatinate.

Modes of Formation.—Mercury may be obtained from the natural sulphides by either roasting the ore, whereby the sulphur is oxidised to sulphur dioxide and the metal liberated, or by distillation in closed retorts with lime, when calcium sulphide and sulphate are formed, and the mercury set free. The first method is almost exclusively employed.

At Idria the crude ore, consisting of cinnabar mixed with shale and earthy matters, is roasted in a furnace, upon perforated arches, n, n'; p, p', Fig. 143. The action of the fire and heated air is to oxidise the sulphur and volatilise the mercury, and the gases and vapours together pass through a series of flues or chambers, C, C, where the mercury condenses.

By the use of a reverberatory furnace (the Alberti furnace), the process can be made continuous The ore is fed into the furnace through a hopper, and the calcined residue is raked out through an opening at the opposite end of the hearth. The gases are passed first through iron pipes kept cool by water, and then through a series of chambers where the remaining metal is condensed.

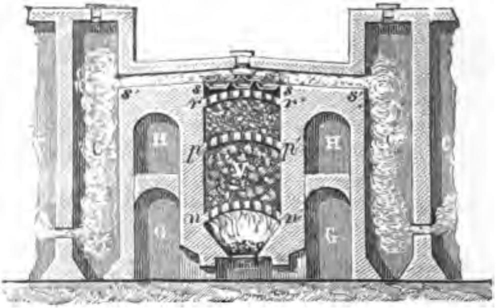

FIG. 143.

The method adopted at Almaden is essentially the same as the Idrian process, except that the condensation takes place in a series of pear-shaped earthenware vessels, called *aludels*, which are connected together as shown in Fig. 144. Usually six rows of forty-seven such aludels are connected with six openings in a chamber immediately above the furnace.

FIG. 144.

The impure mercury is freed from mechanically mixed impurities by straining or filtering through chamois leather, but from metals in solution, such as zinc, tin, lead, and others, it is purified by distillation. For laboratory purposes, pure mercury is best obtained by distillation in vacuo, by means of the apparatus shown in

Fig. 145 (Clarke). In this arrangement the mercury is distilled in a *Sprengel* vacuum. The mercury (previously cleaned by being thoroughly agitated with mercuric nitrate) is placed in the reservoir R, which is then placed upon the upper shelf S, and by means of the clamp, mercury is allowed to pass into the long wide tube T, and up into the bulb. The air in the tube and bulb escapes down the narrow inner tube, which reaches nearly to the top of the bulb, as seen in the enlarged detail, *t*. The mercury is allowed to rise in the bulb and fall down the long inner tube, after the manner of the Sprengel pump. The reservoir is then placed upon the lower adjustable stand, and its height so arranged that the mercury in the bulb falls to the position shown in the figure. This space is a Torricellian vacuum. The mercury is then heated by a ring-burner B, and the whole is protected from draught by the hood *h*.

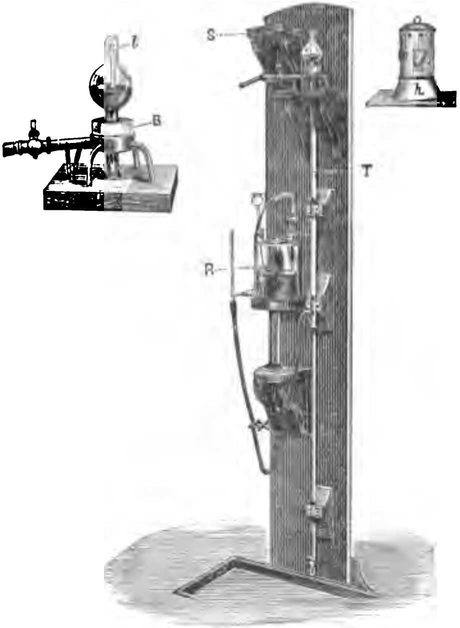

FIG. 145.

As the mercury distils, it passes down the inner tube, and by its fall continues to preserve the Sprengel vacuum within the bulb.

Properties.—At ordinary temperatures mercury is a bright, silver-white liquid metal (hence its old name *quicksilver*, *i.e. live* silver). When cooled to −38.8° it solidifies to a highly crystalline solid, which is ductile and malleable, and softer than lead. When the liquid is cooled it contracts uniformly until the solidifying point is reached, when considerable contraction takes place. Solid mercury, therefore, is denser than the liquid metal, and sinks in it. The specific gravity of liquid mercury at 0° is 13.596, while that of the solid at its melting-point is 14.193. Mercury in extremely thin films appears a violet colour by transmitted light.

Under a pressure of 760 mm. mercury boils at 357.25°, giving a colourless vapour. The density of mercury vapour referred to hydrogen is 100.15; hence this element, like its associates in the family to which it belongs, consists of mono-atomic molecules when in a state of vapour. Mercury gives off vapour even at ordinary temperatures, and a gold leaf suspended over mercury in a stoppered bottle gradually becomes white upon the surface, owing to its amalgamation with the mercurial vapour.

The vapour of mercury is poisonous, giving rise to salivation.

Mercury does not tarnish on exposure to the air, and is unacted upon by a large number of gases; hence this liquid is invaluable to the chemist, affording a means of collecting and measuring gases which are soluble in water.

When submitted to prolonged heating in the air it is slowly converted into the red oxide, which at a higher temperature is again decomposed into its elements.

Mercury is obtained in the form of a dull-grey powder when it is shaken up with oil or triturated with sugar, chalk, or lard. This operation is known as *deadening*, and is made use of in the preparation of mercurial ointment. The grey powder consists simply of very finely divided mercury in the form of minute globules.

Mercury is not attacked by hydrochloric acid. Strong sulphuric acid is without action upon it in the cold, but when heated the metal dissolves, with evolution of sulphur dioxide. Strong nitric acid rapidly attacks it, with formation of mercuric nitrate and oxides of nitrogen. Cold dilute nitric acid slowly dissolves it, forming mercurous nitrate.

Alloys of Mercury.—When mercury is one of the constituents of an alloy the mixture is called an *amalgam*. Most metals will form an amalgam with mercury. In some cases, as with the alkali metals, the union is attended with great rise of temperature. In other cases, as with tin, an absorption of heat takes place.

Sodium and potassium amalgams are obtained by dissolving various amounts of the metals in mercury. In contact with water they are decomposed, hydrogen being evolved and the alkaline hydroxide formed. On this account sodium amalgam is frequently used in the laboratory as a reducing agent. When heated to 440° these amalgams leave behind crystalline compounds, K_2Hg and Na_3Hg, which spontaneously inflame in contact with the air.

Zinc amalgams are only very slowly acted upon by dilute sulphuric acid; therefore, by the superficial amalgamation of the zinc plates used for galvanic batteries, the same result is obtained as though the zinc were perfectly pure (see page 592), and no solution of zinc takes place until the electric circuit is closed.

Tin amalgams are employed for the construction of ordinary mirrors.

Amalgams of gold, and also copper and zinc, are used in dentistry as a filling or stopping for teeth.

Oxides of Mercury.—Two oxides are known, namely, mercurous oxide, Hg_2O, and mercuric oxide, HgO.

Mercurous Oxide, Hg_2O, is obtained as an unstable dark-brown or black powder when sodium hydroxide is added to mercurous chloride. When exposed to the light, or when gently heated, it is converted into mercuric oxide and mercury.

Mercuric Oxide, HgO, is produced in small quantity by the prolonged heating of mercury in contact with air, or by igniting the nitrate. It is prepared on a large scale by heating an intimate mixture of mercuric nitrate and mercury. Obtained by these methods, it is a brick-red crystalline powder; but when sodium hydroxide is added to a solution of a mercuric salt, the oxide is precipitated as an orange-yellow amorphous powder. When heated, mercuric oxide first darkens in colour, and gradually becomes almost black, but returns to its original bright red colour on cooling. At a red heat it is completely decomposed into its elements.

Salts of Mercury.—Two series of salts, corresponding to the two oxides, are known—(*a*) *mercurous salts*, in which two atoms of the hydrogen of the acids are replaced by the divalent radical or double atom (Hg_2); and (β) *mercuric salts*, in which the same amount of hydrogen is replaced by the single divalent atom (Hg). All the mercury salts are poisonous.

(*a*) MERCUROUS SALTS.

Mercurous Chloride, Hg_2Cl_2 (*calomel*), is met with in small quantities as the mineral *horn mercury.* It may be obtained by the addition of sodium chloride or hydrochloric acid to a solution of mercurous nitrate. On a large scale it is usually prepared by heating a mixture of mercuric chloride and mercury, when the mercurous chloride sublimes as a white or translucent fibrous cake.

When a mixture of mercuric sulphate, common salt, and mercury is heated, mercurous chloride is also obtained, thus—

$$HgSO_4 + 2NaCl + Hg = Na_2SO_4 + Hg_2Cl_2.$$

Calomel is perfectly tasteless, and is insoluble in water. When heated it vaporises without fusing. The density of the vapour that is formed by heating mercurous chloride is 117.87, which is half that demanded by the formula Hg_2Cl_2. It has been shown, however, that the compound dissociates when vaporised into mercuric chloride and mercury.* Boiling hydrochloric acid decomposes mercurous chloride into mercury, which separates out, and mercuric chloride, which dissolves.

Mercurous Nitrate, $Hg_2(NO_3)_2$, is deposited in the form of colourless monosymmetric crystals containing $2H_2O$, from a solution of mercury in cold dilute nitric acid. The salt is soluble in water acidulated with nitric acid, but an excess of water causes the precipitation of a basic nitrate having the composition—

$$Hg_2(NO_3)_2, Hg_2O, H_2O \text{ (or } 2Hg_2(NO_3)(HO)),$$

which, on boiling, is converted into mercuric nitrate and mercury. If either this or the normal salt be boiled in the presence of an excess of mercury, a basic nitrate of the composition—

$$3Hg_2(NO_3)_2, 2Hg_2O, 2H_2O \text{ (or } Hg_2(NO_3)_2, 4Hg_2(NO_3)(HO)),$$

is obtained.

Mercurous Sulphate, Hg_2SO_4, is obtained as a white crystalline precipitate when dilute sulphuric acid is added to a solution of mercurous nitrate. It is very slightly soluble in water.

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* Harris and Meyer, *Berichte*, June 1894.

(β) MERCURIC SALTS.

Mercuric Chloride, $HgCl_2$ (*corrosive sublimate*), is formed when chlorine is passed over heated mercury. It is prepared on a large scale by heating a mixture of mercuric sulphate and common salt, a small quantity of manganese dioxide being added to prevent, as far as possible, the formation of mercurous chloride. The mercuric chloride sublimes as a white translucent mass. It dissolves in water to the extent of 6.57 parts in 100 parts of water at 10°, and 54 parts in the same volume of water at 100°, forming an acid solution from which the salt is deposited in long white silky needles. It readily melts, and volatilises unchanged. It dissolves without decomposition in nitric acid and in sulphuric acid, and volatilises unchanged from its solution in the latter acid on boiling.

Mercuric chloride is a violent poison : the best antidote is albumen, with which it forms an insoluble compound. It has also strong antiseptic properties, and on this account is largely used by taxidermists.

With hydrochloric acid, mercuric chloride forms two crystalline double chlorides, $HgCl_2,HCl$ and $2HgCl_2,HCl$; and with the alkaline chlorides it forms a number of similar double salts, of which the ammonium compound, $HgCl_2,2NH_4Cl,H_2O$, was known to the early chemists under the name *sal alembroth.*

Mercuric Iodide, HgI_2.—When mercury and iodine are rubbed together in a mortar, and moistened with a small quantity of alcohol, the red mercuric iodide is formed. It is also obtained by precipitation from a solution of mercuric chloride, upon the addition of potassium iodide. The precipitate first appears yellow, but in a few seconds becomes scarlet.

Mercuric iodide is insoluble in water, but readily dissolves in either mercuric chloride or potassium iodide, and also in alcohol and in nitric acid. From its solutions it is deposited in scarlet tetragonal pyramids.

Mercuric iodide is dimorphous ; when heated to about 150° the scarlet crystals are changed into bright yellow orthorhombic prisms. At ordinary temperatures this yellow form is unstable, and on being lightly touched it is at once retransformed into the red modification. At very low temperatures, however, the yellow variety is the more stable : thus, when the red crystals are exposed to the temperature of evaporating liquid oxygen, they pass into the yellow variety.

Mercuric Nitrate, $Hg(NO_3)_2$, is prepared by boiling nitric acid with mercury, until sodium chloride produces no precipitate with a sample of the liquid. If this solution be evaporated over sulphuric acid, deliquescent crystals are obtained of $2Hg(NO_3)_2,H_2O$, while the mother-liquor has the composition $Hg(NO_3)_2,2H_2O$.

Mercuric nitrate exhibits a great tendency to form basic salts: thus, when this mother-liquor is boiled, the compound $Hg(NO_3)_2, HgO,2H_2O$ is precipitated. When this compound, or the normal nitrate, is treated with an excess of cold water, there is formed the still more basic salt $Hg(NO_3)_2,2HgO,H_2O$.

Mercuric Sulphide, HgS (*cinnabar*).—When mercury and sulphur are triturated together in a mortar, or when excess of sulphuretted hydrogen is passed into a solution of a mercuric salt, mercuric sulphide is obtained as a black amorphous powder. If this be sublimed, it is obtained as a red crystalline substance.

Mercuric sulphide in the red condition is also obtained by digesting the black amorphous product for some hours in alkaline sulphides. A soluble double sulphide is first formed, which when heated is decomposed, with the deposition of red mercuric sulphide. This compound is manufactured on a large scale for use as the pigment *vermilion.*

Mercuric sulphide is insoluble in either nitric, hydrochloric, or sulphuric acid. In the presence of an alkali it is soluble in sodium or potassium sulphide, and deposits crystals from these solutions having the composition $HgS,Na_2S,8H_2O$, and $HgS,K_2S,5H_2O$ respectively.

Ammoniacal Mercury Compounds.—These may be regarded as ammonium salts, in which two atoms of hydrogen in ammonium (NH_4) have been replaced by either (Hg_2) in the *mercurous*, or by (Hg) in the *mercuric* compounds; the two atoms so replaced being either drawn from one and the same ammonium group, or from two.

(*a*) MERCUROUS COMPOUNDS.

Mercurous Ammonium Chloride, $(NH_2Hg_2)Cl$, is the black powder produced by the action of aqueous ammonia upon calomel, thus—

$$Hg_2Cl_2+2NH_3aq=(NH_2Hg_2)Cl+NH_4Claq.$$

Mercurous Ammonium Nitrate, $(NH_2Hg_2)NO_3$, is formed, together with other compounds, when aqueous ammonia is added to mercurous nitrate.

Mercurous Diammonium Chloride, $\left.\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right\}Hg_2$ or $(NH_3)_2Hg_2Cl_2$, is obtained when calomel absorbs dry gaseous ammonia. On exposure to the air it gives up its ammonia, and is reconverted into mercurous chloride.

(β) MERCURIC COMPOUNDS.

Mercuric Ammonium Chloride, $(NH_2Hg)Cl$ (*infusible white precipitate*), is formed when ammonia is added to a solution of mercuric chloride—

$$HgCl_2+2NH_3=(NH_2Hg)Cl+NH_4Cl.$$

Dimercuric Ammonium Chloride, $(NHg_2)Cl$, is obtained by the action of water on the preceding compound.

Mercuric Diammonium Chloride, $\left.\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right\}Hg$, or $(NH_3)_2HgCl_2$ (*fusible white precipitate*), is obtained by adding mercuric chloride to a boiling aqueous solution of ammonium chloride and ammonia, until the precipitate which first forms no longer dissolves. On cooling, the solution deposits small crystals belonging to the regular system.

Oxy-dimercuric Ammonium Iodide, $(NH_2Hg)I,HgO$, is produced by the action of aqueous ammonia upon mercuric iodide, thus—

$$4NH_3+2HgI_2+H_2O=(NH_2Hg)I,HgO+3NH_4I.$$

It is readily produced as a brown precipitate by adding ammonia to a solution of mercuric iodide in potassium iodide containing an excess of potassium hydroxide.

The alkaline solution of potassium mercuric iodide is known as *Nessler's solution*, and constitutes a delicate reagent for detecting the presence of ammonia. Minute traces of free ammonia in solution produce a yellow or brown coloration with this test.

CHAPTER VIII

THE ELEMENTS OF GROUP III

Family A.		Family B.	
Scandium, Sc	44.1	Boron, B	11
Yttrium, Y	89	Aluminium, Al	27.1
Lanthanum, La	138	*Gallium*, Ga	70
Ytterbium, Yb	173	*Indium*, In	115
		Thallium, Tl	204.1

WITH the exception of boron, aluminium, and thallium, the members of this group are amongst the rarest of the elements.* Some of these occur only in minute traces in certain ores of other metals: such is the case with the elements gallium and indium, which are met with in certain specimens of zinc-blende, the ore being considered *rich* in gallium if it contains as much as 0.002 per cent. of this element. Both gallium and indium were discovered by means of the spectroscope; the latter by Reich and Richter (1863), and named indium on account of two characteristic lines in the indigo-blue part of the spectrum; gallium by Lecocq de Boisbaudran (1875), and named after his own country. The spectrum of this metal is characterised by two violet lines. One of the most remarkable properties of gallium is its extremely low fusing-point, the metal melting at 30.15°. (For a comparison of the properties of gallium with Mendelejeff's *eka-aluminium*, see page 124.)

Others of these elements are met with in certain rare minerals, thus, lanthanum occurs in the mineral *orthite* (from Greenland); and both yttrium and lanthanum (associated also with the rare elements cerium and erbium) are found in *gadolinite or ytterbite* (from Ytterby).

Boron (the typical element of the group) is the only non-metal: all the others exhibit well-marked metallic properties. They all yield sesquioxides of the type R_2O_3; in the case of boron this oxide, B_2O_3, is acidic.

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* For detailed descriptions of the rare elements, the student is referred to larger treatises, or to chemical dictionaries.

Thallium in many respects is peculiar. It forms two series of compounds; in one class it functions as a monovalent, and in the other as a trivalent element. In some of its properties it exhibits a close analogy to the alkali metals; thus, it forms a soluble strongly alkaline hydroxide, $TlHO$, corresponding to KHO. And many of its salts, such as the sulphate, Tl_2SO_4; perchlorate, $TlClO_4$, and the phosphates, are isomorphous with the corresponding potassium compounds.

Thallium also shows many properties in common with lead, which in the periodic system is the next element in the series (the fourth long series). Thus, the chloride, like lead chloride, is thrown down as a white curdy precipitate on the addition of hydrochloric acid to a soluble salt of the metal, and like lead chloride, thallous chloride is soluble in hot water. Thallous iodide also closely resembles lead iodide, being formed as a yellow crystalline precipitate when potassium iodide is added to a soluble thallous salt.

Metallic thallium also bears the closest resemblance to metallic lead.

In the *thallic* compounds this element is more closely related to the other members of this family: thus, thallic oxide, Tl_2O_3; thallic chloride, $TlCl_3$; and thallic sulphide, Tl_2S_3, are analogous to the corresponding boron compounds, B_2O_3, BCl_3, B_2S_3.

BORON.

Symbol, B. Atomic weight=11.

Occurrence.—The element boron has never been found in the free state. In combination it occurs principally as boric acid in volcanic steam, and as metallic borates, of which the commonest are *tincal*, a crude sodium borate, or borax, $Na_2B_4O_7,10H_2O$; *boracite* and *colemanite*, or *borate spar*, $Ca_2B_6O_{11}$; and *boronatrocalcite*, or *ulexite*, $Ca_2B_6O_{11},Na_2B_4O_7,16H_2O$.

Modes of Formation.—(1.) Boron may be prepared by heating boron trioxide with either sodium or potassium in a covered crucible—

$$2B_2O_3+6Na=3Na_2O_2+4B.$$

The fused mass is boiled with dilute hydrochloric acid, and the boron, which is in the form of a dark-brown powder, is separated by filtration.

(2.) The element may also be obtained by heating potassium borofluoride with potassium—

$$BF_3,KF+3K=4KF+B.$$

(3.) Boron is also formed when potassium is heated in the vapour of boron trichloride—

$$BCl_3+3K=3KCl+B.$$

Properties.—Boron, as obtained by these methods, is a dark greenish-brown powder. When strongly heated in air it burns, uniting both with oxygen and nitrogen, forming a mixture of boron trioxide, B_2O_3, and boron nitride, BN. It is unacted upon by air at ordinary temperatures.

Boron has no action upon boiling water, but cold nitric acid converts it into boric acid—

$$B+3HNO_3=H_3BO_3+3NO_2.$$

When heated with sulphuric acid it is similarly oxidised—

$$2B+3H_2SO_4=B_2O_3+3SO_2+3H_2O.$$

When fused with alkaline carbonates, nitrates, sulphates, and hydroxides it forms borates of the alkali metals, thus—

$$\begin{aligned}2B+3Na_3CO_3&=2Na_3BO_3+3CO.\\2B+6KHO&=2K_3BO_3+3H_2.\end{aligned}$$

Boron dissolves in molten aluminium, which on cooling deposits crystals of a compound of aluminium and boron.*

Boron Trioxide, B_2O_3, is formed when boron burns in the air or in oxygen. The readiest method for its preparation consists in heating boric acid to redness, when it fuses and gives up water—

$$2B(HO)_3=3H_2O+B_2O_3.$$

Properties.—The fused mass solidifies to a transparent, colour-

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* This compound was at one time mistaken for an allotropic modification of boron.

less, vitreous solid, which gradually absorbs atmospheric moisture and becomes opaque. It is not volatile below a white heat, and on this account, although only a feeble acid, it is capable at high temperatures of displacing strong acids which are volatile from their combinations; thus, when boron trioxide is fused with potassium sulphate, potassium borate is formed and sulphur trioxide expelled—

$$B_2O_3 + 3K_2SO_4 = 2B(KO)_3 + 3SO_3.$$

Boron trioxide at a high temperature is capable of dissolving many metallic oxides, some of which impart to the fused mass a characteristic colour.

Boron forms three oxyacids, namely—

Orthoboric acid, $B(HO)_3$, or H_3BO_3.
Metaboric acid, $B_2O_2(HO)_2$, or $H_2B_2O_4$, or B_2O_3,H_2O.
Pyroboric acid, $B_4O_5(HO)_2$, or $H_2B_4O_7$, or $2B_2O_3,H_2O$.

Orthoboric Acid, or **Boric Acid,** $B(HO)_3$, occurs naturally, both in the waters and in the jets of steam which issue from the ground in many volcanic districts, notably in Tuscany.

The actual amount of boric acid in these natural jets of steam or *soffioni* is very small; but as the steam becomes condensed in the pools of water or *lagoons* which often surround the jets, the amount of boric acid with which the water becomes charged is sufficient to constitute this a profitable source of supply. To obtain the acid, large brick-work basins are built round the steam jets in such a manner that the liquid can be caused to flow from one to another. Water is placed in the highest basin, and after the steam from the fumaroles beneath it has blown through for twenty-four hours the liquid is passed on to the second basin, and a fresh supply of water is run into the first. In this way the water passes on through a series of four or five such basins, receiving the steam of the soffioni for twenty-four hours in each. The muddy liquor, after passing through a settling reservoir, is concentrated by evaporation, the heat from the natural steam being utilised. The concentrated liquor, having a specific gravity about 1.07, is allowed to cool in lead-lined tanks; and the crystals, after being drained, are dried upon the floor of a chamber, also heated by the natural steam. The crude boric acid thus obtained is purified by recrystallisation.

Boric acid may be prepared by the action of sulphuric acid or hydrochloric acid upon a strong solution of borax—

$$Na_2B_4O_7+5H_2O+2HCl=2NaCl+4H_3BO_3.$$

Properties.—Boric acid crystallises in lustrous white laminæ, which are soft and soapy to the touch. 100 parts of water at 18° dissolve 3.9 parts of the acid. The aqueous solution turns blue litmus to a port wine red, similar to the colour produced by carbonic acid. In contact with turmeric paper it gives a brown stain resembling that caused by alkalies, but readily distinguished by not being destroyed by acids and by being turned black in contact with a solution of sodium hydroxide. Boric acid is more soluble in alcohol than in water, and when this solution is boiled a portion of the boric acid volatilises with the alcohol and imparts a green colour to the flame of the burning vapour.

The orthoborates are mostly unstable salts.

Metaboric Acid, $H_2B_2O_4$, is obtained when boric acid is heated to 100°—

$$2H_3BO_3=2H_2O+H_2B_2O_4.$$

The metaborates are more stable salts than the orthoborates. The acid is dibasic, and forms normal and acid salts as well as super-acid salts, thus—

Normal potassium metaborate . .	$K_2B_2O_4$.
Acid potassium metaborate . .	HKB_2O_4.
Super-acid potassium metaborate .	$HKB_2O_4,H_2B_2O_4$.

Pyroboric Acid, $H_2B_4O_7$, is obtained by heating either metaboric acid or orthoboric acid to 140° for some time—

$$2H_2B_2O_4=H_2O+H_2B_4O_7.$$
$$4H_3BO_3=5H_2O+H_2B_4O_7.$$

Borax.—The most important salt of pyroboric acid is the sodium salt, ordinary borax, $Na_2B_4O_7,10H_2O$. This compound occurs naturally as the mineral *tincal.* It is manufactured from boric acid by double decomposition with sodium carbonate—

$$4H_3BO_3+Na_2CO_3=Na_2B_4O_7+6H_2O+CO_2.$$

Anhydrous sodium carbonate is added to a boiling solution of boric acid, and the liquid is then allowed to crystallise, when it forms large transparent prisms belonging to the mono-symmetric system of the composition $Na_2B_4O_7,10H_2O$.

The chief source of borax, however, is furnished by the natural deposits of borate of lime in Bolivia. The powdered mineral is boiled with water, and soda ash is added to the mixture, when calcium carbonate is precipitated, and a mixture of borax and sodium metaborate is formed—

$$Ca_2B_6O_{11}+2Na_2CO_3=2CaCO_3+Na_2B_4O_7+Na_2B_2O_4.$$

On crystallisation the borax deposits, and the more soluble metaborate remains in the mother-liquor. On concentrating these mother-liquors and blowing carbon dioxide through the solution, the metaborate is converted into borax, which is precipitated as a fine meal, leaving sodium carbonate in solution—

$$2Na_2B_2O_4+CO_2=Na_2CO_3+Na_2B_4O_7.$$

When heated, borax loses its water of crystallisation and swells up, forming a white porous mass, which finally melts to a clear glass.

100 parts of water at 10° dissolve 4.6 parts of crystallised borax, and at 100°, 201.4 parts; the solution possesses a feeble alkaline reaction.

When deposited slowly from warm solutions (*i.e.* above about 50° C), borax crystallises in octahedrons having the composition $Na_2B_4O_7,5H_2O$; but when crystallised without any special precautions it forms prismatic crystals containing 10 molecules of water. This is the ordinary form in which borax is met with.

Boron Trifluoride, BF_3, is formed when boron is brought into fluorine; the boron takes fire spontaneously in the gas, forming the trifluoride.

It is also produced when a mixture of dry powdered fluorspar and boron trioxide is heated to redness in an iron vessel, calcium borate being at the same time produced—

$$2B_2O_3+3CaF_2=Ca_3B_2O_6+2BF_3.$$

It is more conveniently prepared by heating together fluorspar, boron trioxide, and sulphuric acid. The reaction may be regarded as taking place in two stages, thus—

$$(1.)\ CaF_2+H_2SO_4=CaSO_4+2HF.$$
$$(2.)\ B_2O_3+6HF=3H_2O+2BF_3.$$

Properties.—Boron trifluoride is a colourless, pungent-smelling gas, which fumes strongly in moist air on account of its powerful affinity for water. So great is this affinity, that a strip of paper introduced into the gas is charred, by the abstraction of the elements of water.

Boron fluoride neither burns nor supports the combustion of ordinary combustibles. When potassium is heated in the gas it burns brilliantly, forming the borofluoride.

At 0° one volume of water dissolves about 1000 volumes of the gas, the absorption being attended with rise of temperature.

When the gas is passed into water until the solution is distinctly acid, a mixture of metaboric acid and hydrofluoboric acid is obtained: the former separates out, while the latter remains in solution—

$$8BF_3+4H_2O=H_2B_2O_4+6HBF_4.$$

When the gas is passed into water until the latter is saturated, a syrup-like liquid is obtained which chars organic matter and is strongly corrosive. This liquid is sometimes called fluoboric acid, and contains boron trifluoride and water in the proportions represented by the formula $2BF_3,4H_2O$; or it may be regarded as consisting of metaboric acid and hydrofluoric acid, as expressed by the formula $H_2B_2O_4,6HF$.* In presence of an excess of water, this substance is decomposed into metaboric acid and hydrofluoboric acid.

When mixed with its own volume of dry ammonia gas, boron fluoride forms a white crystalline compound, having the composition represented by the formula BF_3,NH_3. This substance may be sublimed without change. Two other compounds with ammonia are known, namely $BF_3,2NH_3$, and $BF_3,3NH_3$. These are both colourless liquids, which on being heated give off ammonia, leaving the solid BF_3,NH_3.

The salts of hydrofluoboric acid, HBF_4, are known as *borofluorides* (sometimes *fluoborates*), and are formed by the action of the acid upon metallic hydroxides—

$$HBF_4+KHO=H_2O+KBF_4.$$

In many instances their aqueous solutions redden litmus; this is the case with ammonium borofluoride, NH_4BF_4, and calcium borofluoride, $Ca(BF_4)_2$.

Boron Trichloride, BCl_3, is produced when boron is heated in a stream of dry chlorine.

It is most readily prepared by passing dry chlorine over an intimate mixture of boron trioxide and charcoal, heated to redness in a porcelain tube. The volatile product is condensed in a tube immersed in a freezing-mixture—

$$B_2O_3+3Cl_2+3C=3CO+2BCl_3.$$

---

* It is considered very doubtful whether this substance can be regarded as a definite compound.

Properties.—Boron trichloride is a mobile, colourless liquid, boiling at 18.23. It fumes in moist air, being decomposed in contact with water, with formation of boric and hydrochloric acids—

$$BCl_3+3H_2O=B(HO)_3+3HCl.$$

Boron trichloride unites directly with dry gaseous ammonia, with evolution of considerable heat, forming a white crystalline compound, having the composition $2BCl_3,3NH_3$.

Boron Hydride, BH_3.—This compound has never been obtained in a state of purity. When magnesium boride (an impure substance obtained by fusing boron trioxide and magnesium in a covered crucible) is acted upon by hydrochloric acid, a gas is evolved which has a characteristic and unpleasant smell, and which produces headache and sickness when inhaled. The gas is largely hydrogen, containing, however, a certain quantity of boron hydride, which imparts to the flame a green colour, and produces boron trioxide. When passed through a heated tube, boron is deposited as a brown film. When burnt with a limited supply of air, or when a cold porcelain dish is depressed into the flame of the burning gas, a brown stain of boron is deposited.

Boron Nitride, BN, is formed when boron is strongly heated in nitrogen or in ammonia. It is best obtained by heating, in a covered platinum crucible, a mixture of one part of dehydrated borax, and two parts of ammonium chloride—

$$Na_2B_4O_7+2NH_4Cl=2BN+B_2O_3+2NaCl+4H_2O.$$

Boron nitride is a white amorphous powder. It is insoluble in water, but is slowly acted upon by boiling caustic alkalies, with evolution of ammonia—

$$BN+3KHO=K_3BO_3+NH_3.$$

Heated in a current of steam it forms boron trioxide and ammonia—

$$2BN+3H_2O=B_2O_3+2NH_3.$$

Boron Sulphide, B_2S_3, is prepared by heating a mixture of boron trioxide and carbon (made by mixing boron trioxide and soot with oil, and heating the pellets out of contact with air) to bright redness in a stream of vapour of carbon disulphide—

$$2B_2O_3+3C+3CS_2=6CO+2B_2S_3.$$

Boron sulphide is a yellowish solid, consisting of small crystals. It has a strong unpleasant smell, and its vapour attacks the eyes. It is immediately decomposed by water, being converted into boric acid and sulphuretted hydrogen—

$$B_2S_3+6H_2O=2B(HO)_3+3H_2S.$$

ALUMINIUM.

Symbol, Al. Atomic weight=27.1.

Occurrence.—Aluminium is one of the most abundant of all the elements, although it has never been found in the uncombined state. In combination with oxygen as Al_2O_3, it constitutes such minerals as *corundum*, *ruby*, *sapphire*. As the hydrated oxide, Al_2O_3,H_2O, it occurs associated with iron oxide in the mineral *bauxite*, which constitutes the chief source from which the metal itself is obtained. As a double fluoride of aluminium and sodium, $Al_2F_6,6NaF$, it occurs in the mineral *cryolite*, and as a hydrated phosphate in the various forms of *turquoise*. Aluminium is met with in enormous quantities in the form of silicate, constituting the various *clays*; and as compound silicates in the *felspars*, and other common minerals constituting a large proportion of the solid crust of the earth.

Mode of Formation.—Prior to the advent of the electric furnace as a manufacturing agent, aluminium was obtained from the mineral bauxite by the following method :—The process is conducted in four stages—(1.) and (2.) The preparation of pure aluminium oxide, free from iron. (3.) The preparation of a double chloride of aluminium and sodium. (4.) The reduction of the double chloride by means of sodium.

(1.) The powdered bauxite (usually containing about 50 per cent. of alumina) is mixed with sodium carbonate and heated for five or six hours in a reverberatory furnace, when carbon dioxide is evolved and sodium aluminate is formed—

$$Al_2O_3+3Na_2CO_3=Al_2O_3,3Na_2O+3CO_2.$$

(2.) The sodium aluminate is extracted with water, leaving the iron in the form of insoluble oxide. Through the filtered liquid a stream of carbon dioxide is then passed, which decomposes the sodium aluminate, regenerating sodium carbonate, and precipitating hydrated aluminium oxide—

$$Al_2O_3,3Na_2O+3H_2O+3CO_2=3Na_2CO_3+Al_2O_3,3H_2O.$$

(3.) The purified alumina, after being washed and dried, is mixed with sodium chloride and powdered wood charcoal, and sufficient water added to enable the mixture to be worked up into balls.

These are dried at 150° and then packed into a vertical fireclay cylinder, where they are strongly heated in a stream of chlorine—

$$Al_2O_3 + 3C + 3Cl_2 = 3CO + Al_2Cl_6.$$

The aluminium chloride combines with the sodium chloride present in the mixture, forming the double chloride, $Al_2Cl_6,2NaCl$, which volatilises from the retort, and is condensed in an earthenware receiver as a nearly white crystalline salt, which is almost entirely free from iron.

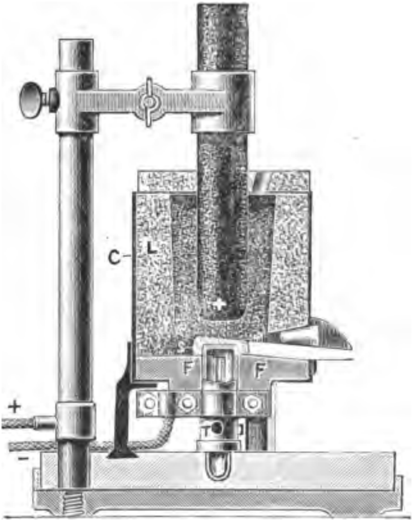

FIG. 146.

(4.) In order to reduce the double chloride, three charges (each consisting of a mixture of 25 kilos of the salt, 11 kilos of powdered cryolite (as a flux), and 12 kilos of metallic sodium in small pieces) are thrown into a strongly heated reverberatory furnace, and are immediately followed by a fourth charge, containing the same quantity of the double chloride and of cryolite, but without sodium. A violent reaction at first takes place, and after a short time the entire mass is in a state of fusion, the metal separating out beneath the slag—

$$Al_2Cl_6,2NaCl + 6Na = 2Al + 8NaCl.$$

Electrolytic Method.—At the present time aluminium is exclusively obtained by means of the electric furnace. The process is an electrolytic one, the electrolyte being a solution of alumina in a bath of molten cryolite. One of the most modern forms of apparatus for the purpose (Borcher's) is shown in section in Fig. 146.

It consists of an iron cylinder or crucible C, with a fireclay bottom F, and thickly lined throughout with alumina, L. The cathode consists of a steel plate S, let into the bottom of the crucible, into which is screwed the copper tube T. To prevent the steel plate from becoming too much heated, and in consequence combining with the aluminium, an arrangement is made to circulate water through the pipe T.

The anode consists of a thick carbon rod, or bundle of rods, which can be raised or lowered at will. A few fragments of aluminium, together with a small quantity of cryolite, is first placed in the crucible, and melted by bringing the anode down upon it. The fused button of aluminium then becomes the cathode. The crucible is then gradually filled up with its charge of cryolite and bauxite until the entire mass is in a molten state. The aluminium oxide alone is decomposed in the process, the oxygen escaping through an opening in the lid, while the metal collects at the bottom and is drawn off at the tap-hole. Fresh bauxite is added in small quantities at a time as the action continues. It is found that the lining of the crucible, although of alumina, is not dissolved to a very great extent, owing to the cooling of the surface by outside exposure to the air.

Properties.—Aluminium is a tin-white metal, possessing great tensile strength. It is very ductile and malleable, but requires frequent annealing during the process of drawing or hammering. Its specific gravity is 2.58; by hammering and rolling it may be raised to 2.68. Its power of conducting heat and electricity is about one-third that of silver. Aluminium is an extremely sonorous metal, and when struck it emits a clear and sustained note. It is not tarnished by air under ordinary circumstances, but when strongly heated it becomes oxidised; and in the condition of thin foil it readily burns in oxygen, forming alumina, Al_2O_3. The metal melts at a temperature about 625°. Aluminium is scarcely acted upon by nitric acid of any strength, but readily dissolves in hydrochloric acid, and in solutions of sodium or potassium hydroxide with elimination of hydrogen. When heated with strong sulphuric acid, aluminium sulphate is formed, and sulphur dioxide is evolved.

Organic acids are almost without action upon aluminium, but in the presence of sodium chloride they are capable of dissolving it to a slight extent. Pure aluminium is scarcely acted upon by water or steam, but the presence of impurities such as usually occur in the commercial metal renders it much more readily oxidised.

Aluminium is a highly electro-positive element, and is capable of reducing a number of other metals from their combinations with oxygen or sulphur. Thus, when finely divided aluminium is heated with the oxides of such metals as manganese, chromium, tungsten, uranium, along with lime to form a slag, an energetic action takes place, in which the aluminium combines with the oxygen, and the metals are thrown out of combination, and are obtained as a coherent mass. Similarly, iron pyrites is reduced to the condition of metallic iron, with the formation of aluminium sulphide.

The extreme readiness with which aluminium is able to effect such reduction, and the exceedingly high temperature which is reached by the action, have led to some useful applications, such as the welding of iron, &c. The property may readily be demonstrated by heating upon a spatula or an iron plate a small quantity of a mixture of powdered aluminium and copper oxide. When such a mixture is brought into a Bunsen flame the action takes place immediately, and is accompanied by an instantaneous and vivid flash of light.

Alloys of Aluminium.—The most important of these is an alloy with copper, containing 10 per cent. of aluminium, and known as *aluminium bronze.* This alloy has a yellow colour, resembling that of gold ; it is scarcely tarnished by exposure to air, and is susceptible of a high polish. Its specific gravity is 7.69, and it possesses a tenacity equal to that of steel, and more than twice that of the best gun-metal. The alloy is malleable, and yields good castings, and on account of its many valuable properties it is employed for a variety of purposes.

Aluminium Oxide (*alumina*), Al_2O_3, occurs native in a colourless crystalline condition as *corundum*, and coloured by traces of various metallic oxides in such precious stones as *ruby*, *sapphire*, and *amethyst.* In a less pure condition, it occurs in large quantities as *emery.* These naturally occurring crystalline forms of alumina are extremely hard, ranking second only to *diamond.* Alumina is obtained in an amorphous condition by igniting either the precipitated hydroxide or ammonia alum, thus—

$$Al_2(HO)_6 = 3H_2O + Al_2O_3.$$
$$Al_2(SO_4)_3,(NH_4)_2SO_4 = 2NH_3 + H_2O + 4SO_3 + Al_2O_3.$$

It is also obtained by the action of carbon dioxide upon sodium aluminate (p. 614). In the crystalline form it is obtained by strongly heating a mixture of aluminium fluoride and boron trioxide—

$$Al_2F_6 + B_2O_3 = Al_2O_3 + 2BF_3.$$

The boron trifluoride volatilises, leaving alumina in the form of rhombohedral crystals. Artificial rubies have been obtained by heating barium fluoride with alumina, and adding a trace of potassium dichromate.

Amorphous alumina is a soft white powder, insoluble in water, but dissolved by acids with the formation of aluminium salts ; after being strongly heated, however, alumina is attacked only with slowness by hydrochloric or sulphuric acid.

Aluminium Hydroxides.—Three hydroxides, or hydrated oxides, are known. Thus, when ammonia is added to a solution of an aluminium salt, a white gelatinous precipitate is obtained, which when dried at 100° consists of the trihydrate, $Al_2O_3,3H_2O$, or $Al_2(HO)_6$. If this be heated to 300° it loses $2H_2O$, and is converted into the mono-hydrate, Al_2O_3,H_2O, or $Al_2O_2(HO)_2$. By the addition of ammonia to a boiling solution of an aluminium salt, and drying the precipitate at 100°, the dihydrate is obtained, $Al_2O_3,2H_2O$, or $Al_2O(HO)_4$.

These compounds are soluble in acids, and all yield the same aluminium salts.

Aluminium hydroxide unites with many soluble organic colouring-matters, and precipitates them from solution as *lakes*. Upon this property depends the use of aluminium salts as *mordants* in dyeing and calico-printing : the colouring-matter being held in the fibres of the material by the aluminium hydroxide, which is previously precipitated upon the fabric.

Aluminates.—Alumina is capable of acting as a feeble acidic oxide : thus, the hydroxides are dissolved by sodium or potassium hydroxide, yielding salts known as aluminates. Certain aluminates occur native, such as *spinelle* (magnesium aluminate), Al_2O_3,MgO, and chrysoberyl (beryllium aluminate), Al_2O_3,BeO.

Sodium aluminate is now manufactured on a large scale, for the preparation of the metal (p. 614) and also of aluminium salts.

It is readily decomposed even by carbonic acid (p. 614), and by aluminium chloride--

$$Al_2O_3,3Na_2O + Al_2Cl_6 = 6NaCl + 2Al_2O_3.$$

On the manufacturing scale powdered cryolite is employed to effect this decomposition, the aluminium hydroxide being precipitated, and the sodium fluoride going into solution—

$$Al_2O_3,3Na_2O + Al_2F_6,6NaF = 12NaF + 2Al_2O_3.$$

Aluminium Sulphate, $Al_2(SO_4)_3,18H_2O$, is found native as the minerals *hair salt* and *aluminite*, the latter being a basic salt

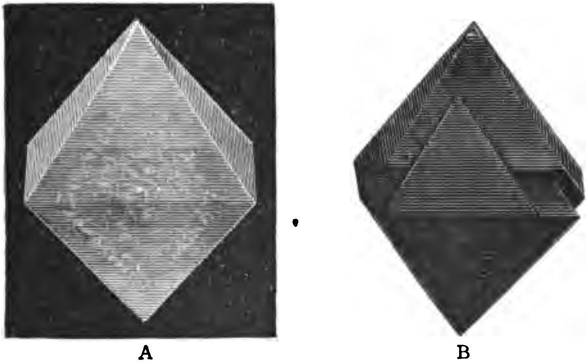

FIG. 147.

having the composition $Al_2O_3SO_3,9H_2O$. The normal sulphate is obtained by dissolving the hydrated oxide in sulphuric acid. Large quantities of commercial aluminium sulphate are made by directly dissolving bauxite in sulphuric acid. The product, however, contains iron, which is detrimental to the technical uses to which the sulphate is applied, and from which therefore it must be carefully purified. Pure aluminium sulphate is prepared from either bauxite or cryolite by first forming sodium aluminate: in the former case by heating the mineral with sodium carbonate (p. 614), and in the case of cryolite by boiling with milk of lime—

$$Al_2F_6,6NaF + 6Ca(HO)_2 = 6CaF_2 + 6H_2O + Al_2O_3,3Na_2O.$$

The sodium aluminate, free from iron, is then decomposed by carbon dioxide, as already described, and the precipitated hydrated oxide dissolved in sulphuric acid. On concentration, the mass solidifies to a white, difficultly crystallisable solid.

The Alums.—Aluminium sulphate unites with certain other sulphates, forming double salts, which belong to a class of compounds known as the alums. The most important of these compounds is the double sulphate of aluminium and potassium, $Al_2(SO_4)_3,K_2SO_4,24H_2O$, known as *potassium alum*, or simply *alum*.

The alums have the general formula $R_2(SO_4)_3,M_2SO_4,24H_2O$, in which R may be either aluminium, iron, chromium, manganese (indium or gallium), and M a monovalent element or group, such as sodium, potassium, or ammonium.

These compounds are all isomorphous, crystallising in the regular system (usually in cubes or octahedra) with twenty-four molecules of water. Fig. 147 represents a crystal of potassium alum (A) and potassium chromium alum (B). In naming the alums* it is usual, when the salt contains *aluminium*, only to introduce the name of the monovalent element or group: thus, *ammonium alum*, or *potassium alum*, signifies the double sulphate of ammonium, or potassium, and aluminium. If, on the other hand, the compound contains no aluminium, the names of both metals are used, thus, *potassium chromium alum*, *ammonium iron alum*.

A second class of double sulphates is known, which resemble the alums, although they are not isomorphous with them. These are termed *pseudo-alums*. They may be regarded as alums, in which the two atoms of the monovalent element are replaced by one atom of a divalent element, thus—

Manganese aluminium, pseudo-alum	$Al_2(SO_4)_3MnSO_4,24H_2O$.
Iron aluminium, pseudo-alum	$Al_2(SO_4)_3FeSO_4,24H_2O$.
Copper iron, pseudo-alum	$Fe_2(SO_4)_3CuSO_4,24H_2O$.
Zinc iron, pseudo-alum	$Fe_2(SO_4)_3ZnSO_4,24H_2O$.
Magnesium manganese, pseudo-alum	$Mn_2(SO_4)_3MgSO_4,24H_2O$.

The alums are all soluble in water, and their solutions have an

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* Selenic acid (the selenium analogue of sulphuric acid) forms a similarly constituted series of double selenates, crystallising in the same form, and with the same number of molecules of water. The system of nomenclature adopted for these compounds is the same: thus, *ammonium selenio-alum* signifies the double selenate of ammonium and aluminium, while *potassium chromium selenio-alum* represents the double selenate of potassium and chromium.

acid reaction and possess an astringent taste. When heated they gradually part with water, and at higher temperatures are broken up into oxides and alkaline sulphates; in the case of ammonium alums, leaving only the metallic oxide.

Potassium Alum, $Al_2(SO_4)_3,K_2SO_4,24H_2O$, is prepared by the addition of the requisite quantity of potassium sulphate to aluminium sulphate. A considerable quantity of alum is also obtained from a naturally occurring basic potassium alum, known as *alum stone*, or *alunite*, which has the composition $Al_2(SO_4)_3$, $K_2SO_4,2Al_2O_3,8H_2O$. At Tolfa this is first calcined, and afterwards lixiviated with water, which dissolves the potassium alum, leaving alumina undissolved. The alum so obtained is known as *Roman alum;* and although it has a reddish colour, due to the presence of iron, this iron is present only as the insoluble oxide, which is readily removed, and the salt is in reality extremely pure.

Alunite is also converted into alum, by treating the calcined mineral with sulphuric acid, and adding the requisite quantity of potassium sulphate. A large quantity of alum is manufactured from *alum shale*, which is a bituminous mineral, consisting chiefly of aluminium silicate, with finely divided iron pyrites disseminated throughout the mass. The shale is usually first roasted, and is then exposed to the action of air and moisture, whereby the oxidation of the pyrites is completed. The result of this oxidation is the formation of sulphuric acid, which, acting upon the aluminium silicate, forms aluminium sulphate, while the iron is converted into ferrous and ferric sulphates, and ferric oxide. The oxidised mass is then lixiviated with water, and, after concentration, the requisite quantity of potassium chloride or sulphate is added to the hot liquor. (The use of potassium chloride is preferable, as by double decomposition the ferrous and ferric sulphates are converted into the very soluble chlorides, and an equivalent amount of potassium sulphate is formed.) The liquor is stirred mechanically during its cooling, whereby the alum is deposited in small crystals known as *alum meal*, which permit of its more ready purification by recrystallisation.

Alum crystallises in fine colourless regular octahedra, which, on exposure to the air, become coated with a white efflorescence, due not to loss of water, but to absorption of atmospheric ammonia, and the formation of a basic salt.

The solubility of alum in water increases rapidly with rise of temperature. Thus, 100 parts of water at 0° dissolve 3.9 parts of alum; at 50°, 44.1 parts; and at 100°, 357.5 parts. Alum is insoluble in alcohol.

When heated to 42°, alum loses 11 molecules of water; and when heated to 61° in a closed vessel over sulphuric acid, it parts with 18 molecules.

On the application of heat, alum first melts in its own water of crystallisation, which is gradually expelled, until at a dull red heat the salt is converted into a white porous mass, known as *burnt alum.* At a still higher temperature it is broken up into potassium sulphate, alumina, and sulphur trioxide. Burnt alum is only very slowly dissolved by water. The chief use of alum is as a mordant in dyeing, alum being a salt which is much more easily obtained in a state of purity than aluminium sulphate. By the addition of sodium hydroxide or carbonate to a solution of alum, until the precipitate first thrown down is just redissolved, a basic alum is produced known as *neutral alum*—

$$2Al_2(SO_4)_3,K_2SO_4+6NaHO=Al_2(SO_4)_3,Al_2(HO)_6,K_2SO_4+\\3Na_2SO_4+K_2SO_4.$$

This solution gives up its alumina to the fabric with great ease, and on this account is used by dyers and calico-printers as a mordant.

When this solution is heated to 40°, ordinary alum is reformed, and a precipitate is obtained consisting of another basic salt, having the same composition as *alunite,* thus—

$$2Al_2(SO_4)_3,Al_2(HO)_6,K_2SO_4=Al_2(SO_4)_3,K_2SO_4)+\\Al_2(SO_4)_3,2Al_2O_3,K_2SO_4+6H_2O.$$

Aluminium Fluoride, Al_2F_6.—This compound may be prepared by passing gaseous hydrochloric acid over a mixture of fluorspar and alumina heated to whiteness in a graphite tube, when aluminium fluoride volatilises, leaving calcium chloride—

$$3CaF_2+Al_2O_3+6HCl=3H_2O+3CaCl_2+Al_2F_6.$$

In the form of a crystalline hydrate it may be obtained by dissolving alumina in aqueous hydrofluoric acid—

$$Al_2O_3+6HF+H_2O=Al_2F_6,7H_2O.$$

Aluminium fluoride forms colourless rhombohedral crystals, which are insoluble in water. It combines with alkali fluorides, forming insoluble double fluorides, of which the sodium compound is the most important, $Al_2F_6,6NaF$. This compound occurs native as the mineral *cryolite.*

Aluminium Chloride, Al_2Cl_6.—This compound is produced when powdered aluminium is strongly heated in chlorine, or with certain metallic chlorides, such as zinc chloride. It is best obtained by passing chlorine over a strongly heated mixture of alumina and charcoal.

An aqueous solution of aluminium chloride may be obtained by dissolving alumina in hydrochloric acid. On evaporation the solution deposits crystals of a hydrate, $Al_2Cl_6,12H_2O$.

Aluminium chloride forms white hexagonal crystals, which fume strongly in moist air. When gently heated it vaporises, and sublimes without fusion. When heated under pressure of its own vapour, the compound melts. It dissolves in water with the evolution of heat, and the solution on evaporation deposits the hydrated chloride, which, on being heated, breaks up into hydrochloric acid, water, and alumina—

$$Al_2Cl_6,12H_2O=6HCl+9H_2O+Al_2O_3.$$

Aluminium chloride unites with other metallic chlorides, forming double salts, of which the sodium compound $Al_2Cl_6,2NaCl$ (page 615) is the most important. It also combines with ammonia, forming the compounds $Al_2Cl_6,6NH_3$ and $Al_2Cl_6,2NH_3$.

Aluminium Sulphide, Al_2S_3.—When finely divided aluminium is heated with iron pyrites, an energetic reaction takes place; metallic iron being reduced, and aluminium sulphide being formed. The same compound is produced when sulphur is thrown upon strongly heated aluminium. As obtained by these methods, aluminium sulphide is a greyish-black solid, which, when thrown into water, is converted into the oxide with evolution of sulphuretted hydrogen—

$$Al_2S_3+3H_2O=Al_2O_3+3H_2S.$$

The compound is decomposed in the same manner by atmospheric moisture when exposed to the air.

THALLIUM.

Formula, Tl. Atomic weight=204.1.

History.—Thallium was discovered by Crookes (1861) in the seleniferous deposit from a sulphuric acid manufactory. In the spectroscopic examination of certain residues obtained in the extraction of selenium from this deposit, the presence of an unknown element was manifested, by the appearance of one bright green line. From its characteristic spectrum, the name *thallium* (signifying a green twig) was given to the element.

Occurrence.—Thallium is found in small quantities in many varieties of iron pyrites, and when these are employed in the manufacture of sulphuric acid, oxide of thallium collects in the flue dust of the pyrites burners. Thallium also occurs associated with copper, selenium, and silver, in the rare mineral *crookesite.*

Mode of Formation.—The metal is obtained by reducing the sulphate, by immersing strips of zinc into the solution. The thallium is deposited upon the zinc, as a spongy or crystalline mass, which is then pressed together and fused beneath potassium cyanide in a crucible.

Properties.—Thallium is a soft heavy metal, resembling lead. It is readily cut with a knife, and leaves a streak when drawn across paper. When preserved out of contact with air it is a tin-white lustrous metal; but on exposure to the air it tarnishes upon its surface, with the formation of black thallous oxide. Its specific gravity is 11.8, and it melts at 290°.

When exposed to air and moisture, or when placed in water which is free to absorb atmospheric oxygen, the metal is slowly converted into thallous hydroxide, which is soluble in water, and imparts to the liquid a strong alkaline reaction. The solution absorbs carbon dioxide, with the formation of thallous carbonate. When heated in the air thallium melts, and rapidly oxidises to thallium trioxide, Tl_2O_3; heated in oxygen it burns, forming the same oxide. It readily burns when heated in chlorine, producing thallous chloride, $TlCl$. The metal is soluble in dilute acids.

Oxides of Thallium.—Two oxides are known, namely, thallous oxide, Tl_2O, and thallic oxide, Tl_2O_3.

Thallous Oxide, Tl_2O, forms as a dark grey film upon the surface of the metal, on exposure to the air. It may also be obtained by heating the hydroxide to 100°. It dissolves in water, forming the hydroxide.

Thallous Hydroxide is obtained by the addition of barium hydroxide to a solution of thallous sulphate, the precipitated barium sulphate being removed by filtration—

$$Tl_2SO_4+Ba(HO)_2=BaSO_4+2TlHO.$$

The solution, on concentration, deposits yellow needle-shaped crystals of $TlHO,H_2O$. Thallous hydroxide is soluble in water, yielding an alkaline solution which gives a brown stain upon turmeric paper. The stain soon disappears, owing to the destruction of the colouring-matter, and is thereby distinguished from the similar stains produced by sodium and potassium hydroxides.

Thallic Oxide, Tl_2O_3, is obtained when thallium burns in the air, or when thallium oxyhydroxide, $TlO(HO)$, is heated to 100°. It forms a dark reddish powder, insoluble in water. In warm dilute sulphuric acid it dissolves, forming thallic sulphate—

$$Tl_2O_3 + 3H_2SO_4 = Tl_2(SO_4)_3 + 3H_2O,$$

but with hot concentrated acid oxygen is evolved, and thallous sulphate formed—

$$Tl_2O_3 + H_2SO_4 = Tl_2SO_4 + O_2 + H_2O.$$

At a red heat thallic oxide is converted into thallous oxide with loss of oxygen.

Thallium Oxyhydroxide, $TlO(HO)$, is formed by the action of potassium hydroxide upon thallium trichloride—

$$TlCl_3 + 3KHO = 3KCl + H_2O + TlO(HO).$$

Thallous Chloride, $TlCl$, is obtained as a white curdy precipitate when hydrochloric acid is added to a solution of a thallous salt. It is considerably more soluble in hot than in cold water: 100 parts of water at 16° dissolve 0.265 part; and at 100°, 1.427 part of thallous chloride.

Thallic Chloride, $TlCl_3$, is formed by passing chlorine through water in which thallous chloride is suspended. The solution so obtained, on evaporation in vacuo, deposits colourless transparent crystals of $TlCl_3,2H_2O$.

When either thallium or thallous chloride is gently heated in a stream of chlorine, a compound is obtained, having the composition $TlCl_3,TlCl$, or Tl_2Cl_4. If this be further heated, it loses chlorine, and is converted into a yellow crystalline compound of the composition $TlCl_3,3TlCl$, or Tl_4Cl_6, thus—

$$2Tl_2Cl_4 = Cl_2 + Tl_4Cl_6.$$

Thallous Oxysalts.—The *sulphate* Tl_2SO_4, and *nitrate* $TlNO_3$, are best obtained by dissolving the metal in the respective acids. Both salts are soluble in water.

Thallous Carbonate, Tl_2CO_3, is prepared by saturating a solution of thallous hydroxide with carbon dioxide. The salt forms long white prismatic (monosymmetric) crystals, which are moderately soluble in water, giving an alkaline solution.

Thallous Phosphate, Tl_3PO_4, is obtained by precipitation from a thallous solution, by the corresponding potassium phosphate. The monohydrogen phosphate, HTl_2PO_4, on being heated to 200°, is converted into pyrophosphate—

$$2HTl_2PO_4 = H_2O + Tl_4P_2O_7,$$

and the dihydrogen salt, on being ignited, yields the metaphosphate—

$$H_2TlPO_4 = H_2O + TlPO_3.$$

Thallic Oxysalts.—The chief of these are thallic sulphate, $Tl_2(SO_4)_3$; and thallic nitrate, $Tl(NO_3)_3$. They are obtained by the action of sulphuric acid and nitric acid respectively upon thallic oxide Tl_2O_3. Thallic sulphate forms colourless crystals of the composition $Tl_2(SO_4)_3,7H_2O$. It is decomposed by excess of water, with precipitation of the hydrated oxide; and when heated yields thallous sulphate, sulphur trioxide, and oxygen—

$$Tl_2(SO_4)_3 = Tl_2SO_4 + 2SO_3 + O_2.$$

Thallic nitrate is deposited in colourless crystals of $Tl(NO_3)_3,8H_2O$, which are decomposed in the presence of much water.

CHAPTER IX

THE ELEMENTS OF GROUP IV

Family A.		Family B.	
Titanium, Ti	48.1	Carbon, C	12.00
Zirconium, Zr	90.6	Silicon, Si	28.4
Cerium, Ce	140.25	*Germanium*, Ge	72.5
Thorium, Th	232.5	Tin, Sn	119
		Lead, Pb	206.9

Family A consists of four rare elements.* Titanium, as the oxide TiO_2, occurs in the three rare minerals—*rutile*, *brookite*, and *anastase*. The metal is extremely difficult to isolate in a pure state, owing to the fact that it unites directly with nitrogen, forming a nitride.

Zirconium is met with as the silicate $ZrSiO_4$ (or ZrO_2,SiO_2) in the mineral *zircon*. Like silicon, it has been obtained in two forms, crystalline and amorphous. The latter variety, when gently heated, burns in the air, while the crystalline variety requires the high temperature of the oxyhydrogen flame for its ignition.

Cerium occurs associated with lanthanum in the rare minerals *cerite* and *orthite*, and with yttrium and ytterbium in *gadolinite* and *wöhlerite*.

Thorium is found in the extremely rare minerals, *thorite* and *orangeite*, met with in Norway.

Family B.—In this family the rare element germanium forms a link between carbon and silicon on the one hand, and tin and lead on the other.

Carbon (the typical element) is essentially non-metallic, and forms an acidic oxide. Silicon approaches more nearly to the metals in its physical properties, but its oxide is still acidic, and but few compounds are known in which silicon functions as a basic element. Germanium is both metallic and non-metallic ; its oxide

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* For descriptions of these rare elements the student is referred to larger treatises.

unites with acids ; and it also combines with alkaline hydroxides, forming germanates corresponding to silicates. Tin is a still more basic element, forming well-marked salts with acids ; but it is also acidic, and with alkalies forms stannates.

Carbon and silicon exhibit a close relationship. They both form allotropes, which correspond in many respects. They both unite with hydrogen, forming the analogous compounds CH_4 and SiH_4 ; and with hydrogen and chlorine they form the similarly constituted compounds, chloroform, $CHCl_3$; and silicon chloroform, $SiHCl_3$.

Tin and lead approach more nearly to each other, especially in their physical properties, than to the other members of the family. They both form compounds, in which the metals function both as divalent and tetravalent elements ; although in the case of lead (as often happens with the heaviest metals of a family), the element exhibits much greater readiness to act in the lower state of atomicity. Until quite recently (1893) no compound was known in which an atom of lead is united with four monovalent atoms, although lead ethide, $Pb(C_2H_5)_4$, had been obtained. Now, however, the compound $PbCl_4$ has been produced, corresponding to $SnCl_4$, which it resembles in many respects ; and still more recently (1894) the tetrafluoride has been obtained.

Carbon, as usual with the typical elements, stands apart from the other members of the family in many of its attributes. Thus, its oxides are both gaseous ; it also forms a vast number of compounds with hydrogen, oxygen, and nitrogen, the study of which constitutes the science of organic chemistry. This element has already been treated in Part II. (page 285).

SILICON.

Symbol, Si. Atomic weight = 28.4.

Occurrence.—Silicon is not known to occur in the uncombined state, although in combination it is the most abundant and widely distributed of all the elements, with the exception of oxygen. In combination with oxygen, as silicon dioxide or *silica*, SiO_2, it occurs as *flint*, *sand*, *quartz*, *rock crystal*, and *chalcedony ;* while in combination with oxygen and such metals as calcium, magnesium, and aluminium, it occurs in clay and soil, and constitutes a large number of the rocks which make up the earth's crust. Silicon, in combination with oxygen, is also met with in the vegetable kingdom, being absorbed by plants from the soil.

Modes of Formation.—(1.) Silicon may be obtained by strongly heating a mixture of potassium silico-fluoride and potassium—

$$K_2SiF_6 + 2K_2 = Si + 6KF.$$

The mass, after cooling, is treated with water, which dissolves the potassium fluoride, leaving the liberated silicon.

(2.) This element may also be prepared by heating sodium in a stream of the vapour of silicon tetrachloride—

$$SiCl_4 + 2Na_2 = Si + 4NaCl.$$

(3.) In an impure state, mixed with magnesium silicide, it may also be obtained by heating a mixture of dry white sand with about four times its weight of dry magnesium powder in a hard glass tube.

As obtained by either of these methods the silicon is in the form of an amorphous, dark-brown powder.

(4.) Silicon is obtained in a crystalline condition by passing a slow stream of the vapour of silicon tetrachloride over aluminium, previously melted in a current of hydrogen ; the volatile aluminium chloride passes on in the stream of gas, and the liberated silicon dissolves in the excess of aluminium—

$$3SiCl_4 + 4Al = 3Si + 2Al_2Cl_6.$$

As the mass cools, silicon is deposited in the form of long, lustrous, needle-shaped crystals.

(5.) The most convenient method for the preparation of crystallised silicon consists in heating in a crucible a mixture of 3 parts of potassium silico-fluoride, 1 part of sodium, and 4 parts of granulated zinc. The regulus so obtained contains crystallised silicon. It is gently heated, and the excess of zinc drained away, the remainder being removed by treatment with acids.

Properties.—**Amorphous Silicon,** as obtained by the reactions Nos. 1 and 2, is a dark-brown amorphous powder, having a specific gravity of 2.15. When heated in the air it burns with the formation of silicon dioxide, which, being non-volatile, coats the particles of the element and protects it from complete oxidation. It burns when heated in a stream of chlorine, with formation of silicon tetrachloride. It is insoluble in water, and in all acids except hydrofluoric acid, in which it dissolves, with the formation of silico-fluoric (or hydrofluosilicic) acid and evolution of hydrogen—

$$Si+6HF=H_2SiF_6+2H_2.$$

On boiling with potassium hydroxide it forms potassium silicate and hydrogen—

$$Si+2KHO+H_2O=K_2SiO_3+2H_2.$$

Crystallised Silicon.—As obtained by reactions Nos. 4 and 5, silicon is a brilliant, steely-grey substance, crystallised in needles derived from the orthorhombic pyramid. The specific gravity of the crystals is 2.34 to 2.49. Crystallised silicon does not burn in oxygen, even when strongly heated; it burns when heated in chlorine, and takes fire spontaneously when brought into fluorine. It is not soluble in any acid except a mixture of nitric and hydrofluoric acids. Crystallised silicon is very hard, being capable of scratching glass. When silicon is exposed to a high temperature, out of contact with air, it becomes denser and harder, and has been obtained in the form of small, steel-grey nodules, showing a crystalline structure, and having a specific gravity as high as 3.0.*

Silicon Hydride, SiH_4.—This compound is evolved at the negative electrode (along with hydrogen) when dilute sulphuric acid is electrolysed, the electrodes consisting of aluminium containing silicon.

In an impure condition, also mixed with hydrogen, this gas may

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* Although silicon in combination is such an abundant element, constituting, as it does, about one-fourth of the total weight of the solid crust of the earth, in the free state it must still be regarded as somewhat of a rarity, and consequently a good deal of uncertainty exists as to its properties. From differences that have been observed in the substance, as obtained by different methods, and from the close analogy that exists between silicon and carbon, it was at one time believed that three allotropes of this element existed, corresponding to those of carbon. Amorphous silicon was considered to represent charcoal. A crystalline substance obtained by Wöhler, by heating potassium silico-fluoride with aluminium, has been regarded as corresponding to graphite, and called *graphitic* silicon; while the octahedral crystals of silicon prepared by reactions 4 and 5 given above (Deville) were thought to be the analogue of diamond; and this substance has, therefore, been called *diamond* or *adamantoid* silicon. There is considerable doubt as to whether the silicon obtained by all these various methods was sufficiently pure to warrant this classification, and this doubt is not diminished by the recently discovered fact that silicon unites with carbon, forming a hard crystalline substance which has received the name *carborundum*.

be obtained by the action of hydrochloric acid upon magnesium silicide—

$$SiMg_2+4HCl=2MgCl_2+SiH_4.$$

(Magnesium silicide for this reaction may be prepared by fusing together in a covered crucible a mixture of dry magnesium chloride 40 parts, dry sodium chloride 10 parts, sodium silico-fluoride 35 parts, and metallic sodium 20 parts.)

Pure silicon hydride is prepared by acting upon triethyl silicoformate with metallic sodium. The mode of action of the sodium is not known; the ethyl silico-formate breaks up into silicon hydride and ethyl silicate—

$$4SiH(OC_2H_5)_3=SiH_4+3Si(OC_2H_5)_4.$$

Properties.—Silicon hydride is a colourless gas. As obtained by the first two methods it inflames spontaneously. The pure gas does not possess this property. Its ignition-point, however, is very low, and if the gas be slightly warmed, or if a jet of it be caused to impinge upon an object a few degrees above the ordinary temperature, the gas at once takes fire and burns with a brightly luminous flame: it is also rendered spontaneously inflammable by reduction of pressure or by admixture with hydrogen. When brought into chlorine the gas takes fire, with formation of silicon chloride and hydrochloric acid.

When treated with an aqueous solution of sodium or potassium hydroxide, silicon hydride is decomposed, giving the alkaline silicate and evolving four times its own volume of hydrogen—

$$SiH_4+2NaHO+H_2O=SiO(NaO)_2+4H_2.$$

Liquid Silicon Hydride, Si_2H_6.—This compound, which has quite recently been discovered,* is obtained by passing the products from the action of dilute hydrochloric acid upon magnesium silicide through a vessel cooled by liquid air or oxygen, and separating the condensed products by fractionation.

Properties.—Liquid silicon hydride is a colourless mobile liquid boiling at +52°. It may be frozen by means of liquid air to a white crystalline solid, melting at −138°. The liquid is spontaneously inflammable in air at the ordinary temperature, burning with a bright white flame and depositing amorphous silicon and silicon dioxide.

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* Moissan and Smiles, *Comptes Rendus*, March 1902.

If a small quantity of the liquid be vaporised into an atmosphere of hydrogen, the hydrogen acquires the property of spontaneous inflammability in contact with the air. Liquid silicon hydride is immediately attacked by an aqueous solution of potash, yielding potassium silicate and hydrogen—

$$Si_2H_6+4KHO+2H_2O=2SiO(KO)_2+7H_2.$$

Silicon Fluoride, SiF_4.—This compound is formed when silicon is brought into fluorine, the silicon taking fire spontaneously in the gas.

It is prepared by the action of sulphuric acid upon a mixture of powdered fluorspar and sand—

$$2CaF_2+2H_2SO_4+SiO_2=2CaSO_4+2H_2O+SiF_4.$$

Properties.—Silicon fluoride is a colourless, fuming gas. It is not inflammable, and does not support combustion. It is decomposed by water into hydrofluosilicic acid and silicic acid, hence the gas cannot be collected over water—

$$3SiF_4+3H_2O=2H_2SiF_6+H_2SiO_3.$$

The silicic acid is precipitated as a gelatinous mass. Each bubble of gas as it comes in contact with the water is at once decomposed, and a little sack-like envelope of silicic acid is formed round it. On filtering the liquid, a solution of hydrofluosilicic acid is obtained. When silicon fluoride is passed over strongly heated silicon, a white powder is obtained having the composition Si_2F_6.

Silicon Chloride, $SiCl_4$, is formed when silicon is heated in a stream of chlorine. Under these circumstances the silicon burns in the gas.

It is obtained by heating an intimate mixture of silica and carbon in a stream of chlorine, and passing the products through a cooled tube—

$$SiO_2+2C+2Cl_2=2CO+SiCl_4.$$

Properties.—Silicon chloride is a colourless liquid which fumes strongly in moist air and boils at 58.3°. It is decomposed by water into silicic and hydrochloric acids—

$$SiCl_4+4H_2O=Si(HO)_4+4HCl,$$

and the silicic acid so formed passes either entirely or in part into the dibasic acid, thus—

$$Si(HO)_4 = SiO(HO)_2 + H_2O.$$

Disilicon Hexachloride (also known as silicon trichloride), Si_2Cl_6, is formed when the vapour of silicon tetrachloride is passed over strongly heated silicon—

$$3SiCl_4 + Si = 2Si_2Cl_6.$$

It may be prepared by gently heating the corresponding iodine compound with mercuric chloride—

$$Si_2I_6 + 3HgCl_2 = Si_2Cl_6 + 3HgI_2.$$

Properties.—Disilicon hexachloride is a mobile, colourless, fuming liquid, which boils at 147° and crystallises at $-1°$. When the liquid is boiled and the hot vapour allowed to escape into the air, it spontaneously ignites.

Silicon forms two compounds with bromine and with iodine corresponding to the chlorides, namely—

$$SiBr_4\,;\ Si_2Br_6\,;\ SiI_4\,;\ Si_2I_6.$$

Silicon Dioxide, SiO_2, occurs in nature in a more or less pure form in a large number of minerals, some of which have already been alluded to as natural compounds of silicon. Silicon dioxide in an amorphous form is met with in the different varieties of *opal*, and in enormous quantities in the deposit known as *kieselguhr*. This substance consists of the remains of extinct diatomaceæ, and is met with in various parts of Germany. In a crystalline condition silica occurs as *quartz* or *rock crystal*, and also in a rarer form as *tridymite*.

Modes of Formation.—(1.) Silicon dioxide is formed when amorphous silicon is burnt in air or oxygen.

(2.) It may be prepared by heating silicic acid, which readily parts with water and leaves pure silicon dioxide as a light white amorphous powder—

$$Si(HO)_4 = SiO_2 + 2H_2O\ ;\ \text{or}$$
$$SiO(HO)_2 = SiO_2 + H_2O.$$

(3.) In minute crystals, silicon dioxide is obtained by strongly heating a solution of an alkaline silicate in a sealed glass tube, whereby a portion of the silica of the glass is dissolved. When this solution is cooled, silicon dioxide is deposited. If the crystallisation takes place above a temperature of 180°, crystals of quartz are obtained; if below this point, it deposits crystals of tridymite, while at ordinary temperatures the silica is deposited in the amorphous condition. Much larger quartz crystals have been obtained by the prolonged heating to 250° of a 10 per cent. aqueous solution of silicic acid (obtained by dialysis) in stout sealed glass flasks.

Properties.—In the crystalline condition as *quartz*, silicon dioxide forms prismatic crystals belonging to the hexagonal system, terminating in hexagonal pyramids. Fig. 148 represents a mass of quartz or rock crystal.

FIG. 148.

The purest forms of rock crystal are perfectly colourless, having a specific gravity of 2.69, and are sufficiently hard to cut glass. When cut and polished, it exhibits a brilliancy not far inferior to that of the diamond, and is occasionally substituted for this gem.

Quartz is often found coloured by the presence of small quantities of impurities, as in the varieties known as *amethyst quartz* and *smoky quartz*, and in great quantities as *milky quartz.*

The variety of silicon dioxide known as *tridymite* is found as minute crystals in cavities in certain specimens of trachytic rocks. The crystalline form of tridymite, although belonging to the hexagonal system, is distinct from that of quartz, and the crystals are frequently met with grown together in the manner known as *twin-crystals.*

Amorphous silicon dioxide, as it occurs in nature, is a translucent substance having a conchoidal or vitreous fracture ; its specific gravity is 2.3. As artificially prepared, it is a soft white powder whose specific gravity is 2.2. At the temperature of the oxy-hydrogen flame, silicon dioxide melts to a transparent glass-like substance which is capable of being drawn out into fine threads resembling spun glass. These fibres possess many valuable properties, and are employed by physicists in delicate instruments of precision.

Silicon dioxide is insoluble in water and in all acids with the exception of hydrofluoric acid. It dissolves in alkalies, and the amorphous powder can be dissolved in a boiling solution of sodium carbonate. Many natural hot springs contain silica held in solution as an alkaline silicate, and on exposure to atmospheric carbon dioxide the silicate is decomposed with the deposition of silica and the reformation of an alkaline carbonate. The enormous quantities of siliceous sinter deposited by geysers at Rotomahama, New Zealand, were formed in this way. When fused with sodium carbonate, silicon dioxide is converted into soluble sodium silicate—

$$SiO_2 + 2Na_2CO_3 = 2CO_2 + Si(NaO)_4.$$

Silicic Acids.—Silicon dioxide is capable of forming weak polybasic acids, but from the readiness with which they give up water it is probable that none have ever been obtained in a state of purity. The compound represented by the formula $Si(HO)_4$ is known as orthosilicic acid, and is tetrabasic. By the loss of one molecule of water it forms metasilicic acid, $SiO(HO)_2$. When hydrochloric acid is added to a solution of an alkaline silicate, a gelatinous precipitate is obtained, which consists of the dibasic acid $SiO(HO)_2$, or H_2SiO_3—

$$SiO(NaO)_2 + 2HCl = SiO(HO)_2 + 2NaCl.$$

If, on the other hand, the solution of alkaline silicate be added cautiously to an excess of hydrochloric acid, the silicic acid remains in solution, and is probably present as orthosilicic acid, $Si(HO)_4$, or H_4SiO_4—

$$SiO(NaO)_2 + 2HCl + H_2O = Si(HO)_4 + 2NaCl.$$

The sodium chloride in the solution may be removed by a process of separation known as dialysis. This process, discovered by Graham, is based upon a property belonging to certain classes of substances, of passing when in solution through certain membranes. The mixture is placed in an apparatus resembling a small tambourine (Fig. 149) (made by stretching either parchment or parchment paper over a wooden hoop), which is then floated upon water. The sodium chloride passes through the membrane, while the silicic acid remains behind in the dialyser as a dilute aqueous solution. Substances in solution which are capable of readily diffusing through such a membrane were termed by Graham *crystalloids;* while others, such as the silicic acid, which either do not pass through or only do so with difficulty, are known as *colloids.*

This aqueous solution of silicic acid may be concentrated by boiling, and further by evaporation in vacuo over sulphuric acid, until it contains about 21 per cent. of tetrabasic silicic acid, or 14 per cent. of silicon dioxide. In this condition it is a tasteless liquid, having a feeble acid reaction. It cannot be preserved, as on standing it solidifies to a transparent gelatinous mass, which has approximately the composition H_2SiO_3.

FIG. 149.

Silicates.—The silicates constitute a large class of important minerals, many of which are of extremely complex composition. Some of the simplest of these silicates are derived from the dibasic and tetrabasic acids already described, while others may be regarded as the salts of a number of hypothetical polybasic silicic acids, derived from metasilicic acid by the gradual elimination of water. Thus, by the withdrawal of one molecule of water from two molecules of metasilicic acid, an acid known as disilicic acid is obtained, having the composition $Si_2O_3(HO)_2$, or $2SiO_2,H_2O$, or $H_2Si_2O_5$—

$$2SiO(HO)_2 = H_2O + Si_2O_3(HO)_2.$$

By the abstraction of one molecule of water from two molecules of orthosilicic acid another disilicic acid is similarly derived—

$$2Si(HO)_4 = H_2O + Si_2O(HO)_6, \text{ or } 2SiO_2,3H_2O, \text{ or } H_6Si_2O_7.$$

By the partial withdrawal of water from three molecules of silicic acid a number of hypothetical trisilicic acids may be derived, such as—

$$3SiO_2,2H_2O \text{ or } H_4Si_3O_8;\ 3SiO_2,5H_2O \text{ or } H_{10}Si_3O_{11};$$
$$3SiO_2,7H_2O \text{ or } H_{14}Si_3O_{13}.$$

Silicates derived from an acid containing one atom of silicon are termed monosilicates; those from acids with two or three atoms of silicon respectively, disilicates and trisilicates.

Thus, the mineral *peridote* is a monosilicate, Mg_2SiO_4.

Serpentine is a disilicate, $Mg_3Si_2O_7$, and

Felspar, or *orthoclase*, is a trisilicate, $Al_2K_2(Si_3O_8)_2$.

TIN.

Symbol, Sn. Atomic weight=119.

Occurrence.—Tin does not occur in nature in the uncombined state.* It is met with chiefly as the oxide SnO_2 in the mineral *tin-stone* or *cassiterite*,† which is found in immense deposits, although in comparatively few localities. It is usually associated with arsenical ores, copper pyrites, wolfram (a tungstate of iron and manganese), and other minerals. Occasionally it is met with in nodules of nearly pure oxide, known as *stream-tin*.

Mode of Formation.—Tin is obtained exclusively from *tin-stone*; and the process with ordinary ore consists of three operations, namely—(1) calcining, (2) washing, (3) reducing or smelting. If the ore be nearly pure tin-stone it may be at once smelted.

The finely crushed ore, after being washed from earthy matters, is calcined in a reverberatory furnace. The sulphur and arsenic pass away as sulphur dioxide and arsenious oxide, and are led into condensing flues, where the arsenic deposits and is collected. The iron and copper are oxidised to oxide and sulphate. This calcination is sometimes conducted in the revolving calciner, shown on page 486. The calcined ore is next washed, whereby copper sulphate is dissolved, and the iron oxide and other light matters are removed. The purified ore is then mixed with powdered anthracite and smelted in a reverberatory furnace—

$$SnO_2+2C=2CO+Sn.$$

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* Metallic tin has been found in Bolivia, but its origin, whether natural or artificial, is doubtful.

† Cassiterides, the ancient name for the British Isles, is derived from the fact that tin-stone was found in large quantities in Devonshire and Cornwall.

The metal so obtained is purified by first heating it upon the hearth of a similar furnace until the more readily fusible tin melts and flows away from the associated alloys; and afterwards by stirring into the molten tin so separated billets of green wood, which results in the separation of a scum or dross carrying with it the impurities.

Properties.—Tin is a bright white metal, which retains its lustre unimpaired in the air. It is sufficiently soft to be cut with a knife, but is harder than lead, although less hard than zinc. At ordinary temperatures it is readily beaten out into leaf (known as tinfoil), and may be drawn into wire; but at temperatures a little below its melting-point (228°) it becomes brittle and may be powdered. Tin may be obtained in the form of crystals by melting a quantity of the metal in a crucible, and when partially solidified pouring out the remaining liquid portion. Its crystalline character is also seen by pouring over the surface of a block of cast tin or a sheet of ordinary tinned iron a quantity of warm dilute *aqua regia*, when the surface of the metal will immediately exhibit a beautiful crystalline appearance.

When a bar of tin is bent it emits a faint crackling sound, and if quickly bent backwards and forwards two or three times the metal becomes perceptibly hot at the point of flexure. These phenomena are due to the friction of the crystalline particles. Ordinary tin has a specific gravity about 7.2; but if the metal be exposed to the prolonged influence of very low temperatures, it loses its crystalline character and appears of a grey colour. In this condition its specific gravity is 5.8; and it is believed to be an allotropic modification of the element. When strongly heated tin takes fire and burns, forming stannic oxide, SnO_2. It is oxidised by both sulphuric and nitric acids; thus, when heated with strong sulphuric acid, stannous sulphate and sulphur dioxide are produced—

$$Sn + 2H_2SO_4 = SnSO_4 + SO_2 + 2H_2O.$$

The strongest nitric acid (specific gravity, 1.5) is without action upon tin. Ordinary concentrated nitric acid (specific gravity, 1.24) attacks it with violence, forming metastannic acid (page 640), while in cold dilute acid it slowly dissolves with the production of stannous nitrate—

$$4Sn + 9HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_3.$$

The ammonia unites with another portion of nitric acid, forming ammonium nitrate. Strong hydrochloric acid converts it into stannous chloride, with evolution of hydrogen.

Tin is extensively employed in the process of *tinning*, which consists in coating other metals with a thin film of tin by dipping into a bath of the molten metal. Ordinary tin-plate (or in common parlance, "tin," the material of which articles generally called "tins" are made) is thin sheet-iron which has been thus superficially coated with tin.

Alloys of Tin.—Tin enters into the composition of a large number of useful alloys. With lead, tin will mix in all proportions, and many alloys are in use consisting of these two metals. They are all white, and melt at temperatures lower than that of either constituent.

Pewter contains 3 parts of tin to 1 part of lead. Common *solder* consists of 1 part tin and 1 part lead, while coarse and fine solder contain half and twice this proportion of tin respectively. With copper, the most important alloys are the various brasses and bronzes. Britannia metal contains tin 84 parts, antimony 10 parts, copper 4 parts, and bismuth 2 parts. Tin is a constituent also of the so-called *fusible alloys* (see Bismuth, page 500).

Oxides of Tin.—Two oxides are definitely known, namely, stannous oxide, SnO, and stannic oxide, SnO_2. The monoxide is a base, yielding the *stannous salts*; the dioxide is both a basic and an acidic oxide.

Stannous Oxide, SnO, is obtained by heating stannous oxalate out of contact with air, thus—

$$SnC_2O_4 = SnO + CO_2 + CO.$$

When sodium carbonate and stannous chloride are mixed, carbon dioxide is evolved, and the white hydrated oxide is precipitated, thus—

$$2SnCl_2 + 2Na_2CO_3 + H_2O = 4NaCl + 2CO_2 + 2SnO,H_2O.$$

When this hydrated oxide is boiled with insufficient caustic alkali to dissolve it, the undissolved portion is dehydrated and converted into the black monoxide.

When heated in the air, stannous oxide becomes incandescent, burning to the dioxide. It is soluble in acids, forming stannous salts. The solution of stannous oxide in sodium hydroxide is used by the calico-printer, and is known commercially as *sodium stannite.*

Stannic Oxide, SnO_2 (*tin dioxide*), is the chief ore of tin. It is formed where the metal is burnt in the air, but is most readily prepared by igniting metastannic acid.

It is a white amorphous powder, which changes to yellow and brown on heating, but returns to its original condition on cooling. When strongly heated in a stream of gaseous hydrochloric acid, it may be obtained in small crystals, identical with the natural compound. Stannic oxide is unacted upon by acids or alkalies, but in contact with fused potassium hydroxide it is converted into potassium stannate.

Stannic Acid, H_2SnO_3, or SnO_2,H_2O, is obtained in a hydrated condition, as a white gelatinous precipitate, when calcium carbonate is added to stannic chloride in insufficient quantity for complete precipitation. When the precipitate is dried in vacuo, it has the composition H_2SnO_3. The equation representing its formation may be expressed thus—

$$2CaCO_3 + SnCl_4 + H_2O = 2CaCl_2 + 2CO_2 + H_2SnO_3.$$

Stannic acid forms a number of salts, of which sodium and potassium stannates are the most important—the former being extensively employed as a mordant in dyeing, under the name of *preparing salt.* The salts have the composition $Na_2SnO_3,3H_2O$, and $K_2SnO_3,3H_2O$ respectively, and are both soluble in water.

Metastannic Acid, $H_{10}Sn_5O_{15}$, is obtained as a white amorphous powder when tin is acted upon by strong nitric acid; the reaction may be represented thus—

$$5Sn + 20HNO_3 = H_{10}Sn_5O_{15} + 5H_2O + 20NO_2.$$

The composition of the compound depends upon the particular temperature at which it is dried. This acid is sometimes regarded as a polymer of stannic acid, which may be expressed by the formula $5(H_2SnO_3)$; metastannic acid, however, appears to be dibasic, forming salts in which two only of the hydrogen atoms are replaced; its composition may therefore be conveniently expressed thus—

$$H_2SnO_3,4SnO_2,4H_2O, \text{ or } H_2Sn_5O_{11},4H_2O.$$

Potassium and sodium metastannates are the best known salts, their formulæ being—

$$K_2SnO_3,4SnO_2,4H_2O, \text{ and } Na_2SnO_3,4SnO_2,4H_2O.$$

Stannous Chloride, $SnCl_2$, is obtained by dissolving tin in hydrochloric acid, and evaporating the solution, when monosymmetric prisms separate out, having the composition $SnCl_2,2H_2O$. When dried in vacuo they become anhydrous. The anhydrous chloride is directly obtained when tin filings and mercuric chloride are heated together—

$$HgCl_2 + Sn = SnCl_2 + Hg.$$

The reduced mercury volatilises and leaves the chloride, which at a higher temperature may be distilled.

Stannous chloride dissolves in a small quantity of water, but with an excess of water, or on exposure to the air, an oxychloride (or basic chloride) is precipitated, with simultaneous elimination of hydrochloric acid, thus—

$$2SnCl_2 + 2H_2O = SnCl_2,SnO,H_2O + 2HCl.$$

The composition of this oxychloride may also be expressed by either of the following formulæ—

$$Sn_2OCl_2,H_2O, \text{ or } 2Sn(OH)Cl, \text{ or } 2(SnO,HCl).$$

Stannous chloride is a powerful reducing agent, as it readily combines with either oxygen or chlorine; thus, when added to a solution of mercuric chloride, the latter is first reduced to mercurous chloride, which, on being gently warmed, is reduced to metallic mercury—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

By the absorption of oxygen, the above oxychloride and stannic chloride are formed, thus—

$$3SnCl_2 + O + H_2O = SnCl_2,SnO,H_2O + SnCl_4.$$

Stannous chloride boils at a temperature about 606°. The density of the vapour only agrees with the formula $SnCl_2$ at temperatures above 900°, at lower temperatures its vapour-density approaches more nearly to that required by the formula Sn_2Cl_4.

Stannic Chloride, $SnCl_4$, is obtained by passing a stream of dry chlorine over melted tin in a glass retort, or by heating a mixture of powdered tin with an excess of mercuric chloride, when the anhydrous chloride distils over as a colourless, mobile, fuming liquid, which boils at 113.9°. It unites with water with evolution of heat, forming hydrated compounds of the composition $SnCl_4,3H_2O$; $SnCl_4,5H_2O$, and $SnCl_4,8H_2O$. The compound containing $5H_2O$ is employed as a mordant, and is commercially known as *oxymuriate of tin.*

Stannic chloride combines with alkaline chlorides, forming double chlorides (sometimes called *chloro-stannates*), such as $SnCl_4,2NH_4Cl$, and $SnCl_4,2KCl$.

Stannous Sulphide, SnS.—When tinfoil is introduced into sulphur vapour the metal takes fire, and yields a leaden-coloured mass of stannous sulphide.

In the hydrated condition stannous sulphide is precipitated as a brown powder when sulphuretted hydrogen is passed through stannous chloride ; on drying, this becomes black and anhydrous.

Stannous sulphide dissolves in hot concentrated hydrochloric acid. It is also soluble in alkaline polysulphides, forming thiostannates, thus—

$$(1)\quad 4SnS + K_2S_5 = K_2SnS_3 + 3SnS_2.$$
$$(2)\quad SnS_2 + K_2S = K_2SnS_3.$$

On the addition of hydrochloric acid to the solution, *stannic* sulphide is precipitated—

$$K_2SnS_3 + 2HCl = 2KCl + H_2S + SnS_2.$$

Stannic Sulphide, SnS_2.—This compound cannot be formed by heating tin and sulphur alone, as the heat of the reaction is greater than that at which stannic sulphide is resolved into stannous sulphide and sulphur. It is obtained by heating tin amalgam, sulphur and ammonium chloride, in a retort. The action that takes place is a complicated one, various products being volatilised, and stannic sulphide remaining in the retort as a mass of golden-yellow scales. Amongst the products expelled during the process are ammonium chloride, sulphur, mercuric chloride, mercuric sulphide, and sulphuretted hydrogen. The ammonium chloride present probably acts by the formation of ammonium stannous chloride, as an intermediate product, which is then decomposed with the production of stannic sulphide and ammonium stannic chloride thus—

$$2SnCl_2,2NH_4Cl + 2S = SnS_2 + NH_4Cl + SnCl_4,2NH_4Cl.$$

Stannic sulphide is a golden yellow crystalline substance which, when heated, partially sublimes as such, but is for the most part decomposed into the monosulphide and free sulphur. It is largely used as a pigment known as *mosaic gold.*

LEAD.

Symbol, Pb. Atomic weight = 206.9.

Occurrence.—Lead has been found in small quantities in the uncombined state, probably reduced from its ores by volcanic action.

In combination with sulphur it occurs in enormous quantities in the mineral *galena*, PbS, which is the ore from which the metal is chiefly obtained. Large quantities are also met with as carbonate in the mineral *cerussite*, $PbCO_3$. Other natural compounds are *anglesite*, $PbSO_4$; *lanarkite*, $PbSO_4,PbO$; *matlockite*, $PbCl_2,PbO$; *pyromorphite*, $3Pb_3P_2O_8,PbCl_2$.

Modes of Formation.—Lead is very readily reduced from its compounds, and on this account was one of the earliest known metals. It was termed by the Romans *plumbum nigrum.*

Two general processes are made use of for the reduction of lead from its ores :—

In the first method (known as the *reduction process*) the lead sulphide is reduced by double decomposition with lead oxide and sulphate, which are formed by roasting the ore.

In the second (called the *precipitation process*) the sulphide is reduced by metallic iron.

(1.) The galena is introduced into a reverberatory furnace, where it is partially roasted, whereby a portion of the sulphide is oxidised to sulphate and oxide—

$$PbS + 2O_2 = PbSO_4.$$
$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

The temperature is then raised, when the oxide and sulphate react upon a further portion of the sulphide, with the formation of metallic lead and the evolution of sulphur dioxide—

$$PbSO_4 + PbS = 2Pb + 2SO_2.$$
$$2PbO + PbS = 3Pb + SO_2.$$

This method of lead smelting is followed when the ore is fairly free from other metallic sulphides. The reverberatory furnace usually employed (known as the *Flintshire furnace*) has a considerable depression, or well, in the hearth, where the metallic lead collects during the process, and from which it is drawn off into a metal pot.

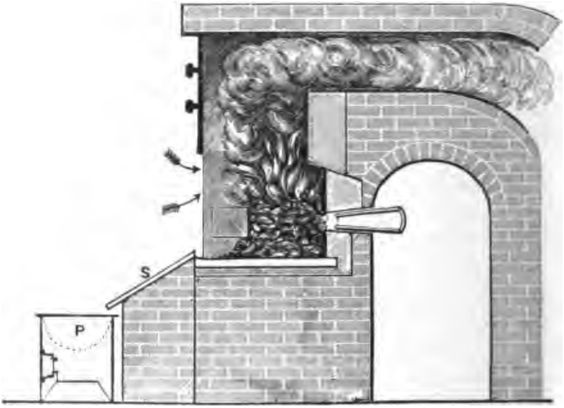

FIG. 150.

The same process is carried out in the North of England, and in Scotland, where a very pure lead ore is employed, upon open shallow hearths (known as the *ore hearth*, or *Scotch hearth*), built under a brickwork hood or chimney in such a manner that the fumes of lead which escape are caused to pass into condensing chambers. Fig. 150 shows such a hearth in section. The fire of peat and coal is urged by a small blast admitted from behind, and the ore is added in small quantities at a time. The reduced metal, sinking to the bottom, runs under the fire-bar and overflows from the shallow hearth down a channel upon an inclined stone surface S (called the *work-stone*), into an iron pot P, which is gently heated by a small fire to enable the operator to ladle the metal out into moulds.

(2.) This method of lead smelting depends upon the fact that at a high temperature metallic iron, in contact with lead sulphide, is converted into ferrous sulphide, with separation of lead—

$$PbS + Fe = FeS + Pb.$$

The ores (either in the raw state, or after previous calcination) are smelted in a blast-furnace with coke and either metallic iron or such materials as will yield iron under the furnace conditions. The sulphide of iron, along with other metallic sulphides, rises to the top of the molten lead as a matt or regulus, while above this a fusible slag collects, consisting chiefly of silicate of iron.

The lead first obtained by any of these processes usually contains antimony, tin, copper, and other metals. These impurities are removed by heating the metal in a shallow, flat-bottomed reverberatory furnace. Most of the admixed metals oxidise before the lead, and collect in the dross which forms upon the surface. This process is known as the *softening of lead*. The silver, however, which is always present, is not removed by this operation, but is extracted by one of the methods for desilverising lead described under silver, page 560.

Properties.—Lead is a soft, bluish-white metal, which when freshly cut exhibits a bright metallic lustre. On exposure to the air its bright surface becomes quickly covered with a film of oxide. Lead is sufficiently soft to be scratched with the finger nail, and it leaves a black streak when drawn across paper. It cannot be hammered into foil or drawn into wire, but may readily be obtained in these forms by rolling and pressing. When a quantity of melted lead is allowed partially to resolidify, and the still liquid portion poured off, the metal is obtained in the form of octahedral crystals belonging to the regular system. Its crystalline nature is also readily seen by submitting a solution of a lead salt to electrolysis, when the metal is deposited upon the negative electrode in beautiful arborescent crystals with a brilliant metallic lustre (Fig. 151). It is deposited in a similar form, known as the *lead tree*, by suspending a strip of zinc in such a solution. The specific gravity of lead is 11.3; it melts at 330° to 335°, and becomes covered with a black film of the suboxide, Pb_2O: when more strongly heated it is oxidised to the monoxide, PbO.

Lead is rapidly dissolved by nitric acid, but hydrochloric and sulphuric acids are almost without action upon it in the cold. Hot concentrated hydrochloric acid, however, slowly converts it into lead chloride.

Lead is unacted upon by pure water in the absence of air; but in contact with air lead hydroxide is formed, which is slightly soluble in water. By the action of atmospheric carbon dioxide upon this solution, a basic carbonate is precipitated, having the composition $2PbCO_3,Pb(HO)_2$. The solvent action of water upon lead is greatly influenced by the presence of various dissolved substances in the water; thus, water containing small quantities of ammoniacal salts, notably the nitrate, dissolves lead much more rapidly, and the same is the case with water charged with carbon dioxide under pressure. In the latter case the action is probably due to the formation of a soluble acid carbonate.

FIG. 151.

Water, on the other hand, containing small quantities of phosphates and carbonates, especially the acid calcium carbonate, are almost entirely without action upon lead. Certain drinking waters (such as the Loch Katrine water), which on account of their purity exert a solvent action upon the lead pipes through which they are conveyed, are rendered incapable of acting upon the lead by being first filtered through chalk or animal charcoal, which enables them to take up sufficient calcium carbonate or phosphate to prevent this action.

On account of the exhaustive methods of desilverisation to which the lead is subjected, commercial lead possesses a degree of purity not found in any other metal as commonly met with; the total amount of foreign metals present in ordinary commercial lead ranges from 0.1 to 0.006 per cent.

Lead is put to a large number of uses in the arts, on account of the ease with which it can be worked, and its power of resisting the action of water and many acids. In the manufacture of lead pipes advantage is taken of the extreme softness of the metal and the readiness with which it can be pressed into shape; the lead, in a pasty or semi-molten condition, being merely squeezed, or *squirted*, through a steel die by hydraulic pressure.

Lead bullets are also made by squeezing the metal into moulds; for as lead contracts on solidification, bullets made by casting always contain a small cavity, which (unless it happens to form exactly at the point of centre of gravity) renders the flight of the bullet untrue.

Oxides of Lead.—Five oxides of lead are known, having the composition Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2.

Lead Suboxide (*plumbous oxide*), Pb_2O, is the black compound which is formed when lead is heated to its melting-point. It is obtained by heating plumbic oxalate to about 300° in a glass tube or retort—

$$2PbC_2O_4 = CO + 3CO_2 + Pb_2O.$$

When heated in the air it burns, forming plumbic oxide; in the absence of air it is decomposed into the same oxide and metallic lead, the reactions being—

$$Pb_2O + O = 2PbO.$$
$$Pb_2O = Pb + PbO.$$

In contact with acids it decomposes in the same manner, lead being deposited, and the plumbic oxide dissolving in the acid to form a plumbic salt.

Plumbic Oxide (*lead monoxide*, *litharge*, *massicot*), PbO, is formed when lead is strongly heated in the air, and is obtained in large quantities in the cupellation of argentiferous lead. It may be obtained by heating lead nitrate or carbonate, and it is produced when any of the other oxides are heated.

Plumbic oxide is a yellowish powder, known commercially as *massicot*, which, when melted and resolidified, is obtained as a crystalline mass, known as *litharge*. Plumbic oxide is very slightly soluble in water, 1 part dissolving in 7000 parts of water: this solution is alkaline, and on exposure to the air absorbs carbon dioxide, forming an insoluble basic carbonate. Plumbic oxide is dissolved by acids, with formation of the salts of lead; it also dissolves in warm potassium or sodium hydroxide.

This oxide forms two hydrated compounds, having the composition $2PbO,H_2O$ and $3PbO,H_2O$. The former is obtained as a white precipitate when ammonia is added to a solution of lead acetate; the second, by the action of ammonia on basic lead acetate at 25°.

Lead Sesquioxide, Pb_2O_3, is obtained as an orange-coloured precipitate by adding sodium hypochlorite to a solution of plumbic oxide in potassium hydroxide. Heat decomposes it into oxygen and plumbic oxide. Acids convert it into the monoxide and dioxide, the former dissolving and yielding a salt of lead. This oxide may be regarded as a compound of two oxides, PbO,PbO_2.

Triplumbic Tetroxide (*red lead*, *minium*), Pb_3O_4, is obtained when lead carbonate, or monoxide, is subjected to prolonged heating in contact with air, at a temperature not above 450°. At higher temperatures it again gives up oxygen. It is a scarlet crystalline powder, varying somewhat in colour, according to its mode of preparation. Dilute acids convert it into PbO_2 and $2PbO$, the latter oxide dissolving to yield lead salts. With strong hydrochloric acid and sulphuric acid the molecule of lead dioxide is acted upon, with evolution of chlorine and oxygen respectively—

$$Pb_3O_4+8HCl=4H_2O+3PbCl_2+Cl_2.$$
$$Pb_3O_4+3H_2SO_4=3H_2O+3PbSO_4+O.$$

When red lead is added in small quantities at a time to hot glacial acetic acid, it dissolves entirely in the acid, and the liquid contains lead tetracetate—a salt which is of interest as being one of the few salts known containing tetravalent lead (see page 628). On cooling, the tetracetate separates out as pale greenish-white needles. The salt is immediately decomposed by water; if therefore the acid solution of it be poured into water, a brown precipitate of lead peroxide is thrown down, and acetic acid regenerated—

$$Pb(C_2H_3O_2)_4 + 2H_2O = PbO_2 + 4H{\cdot}C_2H_3O_2.$$

Red lead* is employed as a pigment, and also in the manufacture of flint glass.

Plumbic Peroxide (*lead dioxide*), PbO_2, may be obtained by the action of dilute nitric acid upon red lead—

$$Pb_3O_4 \text{ (or } PbO_2,2PbO) + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

Or it may be prepared by the action of oxidising agents upon the monoxide. Thus, when chlorine is passed through an alkaline solution, in which the monoxide is suspended, or when bleaching-powder is added to a solution of lead acetate, the dioxide is produced.

The dark-brown deposit which forms upon the positive electrode when a solution of a lead salt is electrolysed, also consists of the dioxide.

Plumbic peroxide is a brown or puce-coloured powder. It is a powerful oxidising substance, and when gently rubbed with flowers of sulphur in a warm mortar the mass suddenly inflames. When a stream of sulphur dioxide is passed over the peroxide in a tube, the two compounds unite to form lead sulphate, the mass becoming incandescent. Nitric acid is without action upon it, but hydrochloric and sulphuric acids act upon it in the same manner as upon red lead. When strongly heated the peroxide gives up oxygen, and is converted into the monoxide.

When plumbic peroxide is boiled with strong aqueous potassium hydroxide it dissolves, and the solution deposits crystals of potassium plumbate, $K_2PbO_3,3H_2O$. This compound corresponds with potassium stannate, $K_2SnO_3,3H_2O$, and its existence shows that lead possesses, although to a very feeble extent, the acidic properties exhibited by the other members of the same family of elements.

Plumbic Chloride (*lead dichloride*), $PbCl_2$, is obtained as a white curdy precipitate when hydrochloric acid, or a soluble chloride, is added to a solution of a lead salt. It is also produced

---

* Commercial red lead varies considerably in composition, and although it has been shown that a definite compound exists of the composition Pb_3O_4 (which may also be expressed by the formula $2PbO,PbO_2$), it is still uncertain whether there are not other compounds consisting of these two oxides united in different proportions.

by the action of boiling hydrochloric acid upon lead in the presence of air. It is best prepared by dissolving lead oxide or carbonate in hot hydrochloric acid, when the lead chloride separates out on cooling in long white, lustrous, needle-shaped crystals belonging to the rhombic system. Lead chloride is soluble in boiling water to the extent of about 4 parts in 100 parts of water. On cooling the solution the greater part of the salt separates out, and at 0° the liquid contains 0.8 part in solution. The presence of hydrochloric acid and soluble chlorides diminishes the solubility of lead chloride.

When heated in contact with air it is converted into an oxychloride, of the composition Pb_2OCl_2, or $PbCl_2,PbO$, corresponding with the natural compound *matlockite*. This compound, in the hydrated condition, Pb_2OCl_2,H_2O, is prepared on a large scale by the addition of lime-water to a solution of lead chloride, and is employed as a white pigment, known as *Pattinson's white lead.*

Cassel yellow is an oxychloride of lead of the composition $PbCl_2,7PbO$, obtained by heating lead oxide and ammonium chloride.

Lead Tetrachloride (*lead perchloride*), $PbCl_4$.—When plumbic peroxide is dissolved in cold concentrated hydrochloric acid, a yellow liquid is obtained, which, on warming, yields chlorine, with precipitation of lead dichloride. This liquid contains the tetrachloride of lead in solution.

When lead dichloride is suspended in hydrochloric acid, and chlorine is passed through the mixture, a solution of lead tetrachloride is obtained; and on the addition of ammonium chloride, ammonium plumbic chloride, $PbCl_4,2NH_4Cl$ (corresponding to ammonium stannic chloride), separates out. When this compound is acted upon with strong sulphuric acid, in the cold, lead tetrachloride separates out as a yellow oily liquid.

Lead tetrachloride is a yellow, highly-refracting, fuming liquid, which decomposes in contact with moisture into lead dichloride and chlorine. It may be preserved beneath concentrated sulphuric acid. With small quantities of water it forms a hydrated compound, but excess of water decomposes it into hydrochloric acid and lead peroxide—

$$PbCl_4+2H_2O=PbO_2+4HCl.$$

When heated with strong sulphuric acid to about 105°, it suddenly decomposes with explosion.

Lead Nitrate, $Pb(NO_3)_2$, is obtained by dissolving litharge in nitric acid. The salt is deposited from the solution in the form of regular octahedral crystals. It is soluble in water to the extent of 50 parts in 100 parts of water at the ordinary temperature. When heated it evolves nitrogen peroxide and oxygen, leaving plumbic oxide (page 242).

On boiling an aqueous solution of lead nitrate with lead oxide, the latter dissolves, and the solution on cooling deposits crystals of a basic nitrate, $Pb(NO_3)HO$ or $Pb(NO_3)_2,PbO,H_2O$. By the addition of ammonia to a solution of lead nitrate, other basic nitrates are obtained, which may be regarded as consisting of compounds of $Pb(NO_3)HO$ with PbO, or of $Pb(NO_3)_2$ with PbO and H_2O in varying proportions.

Lead Carbonate, $PbCO_3$, is obtained as a white crystalline powder by the addition of ammonium sesquicarbonate to a solution of lead nitrate. It occurs in the form of transparent rhombic crystals in the mineral *cerussite*, isomorphous with arragonite. Lead carbonate is almost insoluble in water, but is appreciably dissolved in water charged with carbon dioxide. When sodium or potassium carbonate is added to a solution of lead nitrate, basic carbonates of lead are precipitated, varying in composition with the conditions of temperature. The most important of the basic carbonates is *white lead*, $2PbCO_3,Pb(HO)_2$. This compound is manufactured on a large scale by several processes for use as a pigment. The oldest process, and that which yields the best product, is known as the *Dutch method.* It depends upon the action of acetic acid upon metallic lead, in the presence of moist air and carbon dioxide. The lead, cast into rough gratings in order to expose a large surface, is placed in earthenware pots, as shown in Fig. 152. A small quantity of dilute acetic acid (in the old Dutch process, *vinegar*) is placed in the pots, and the gratings of lead, which rest upon the shoulder of the pot, are piled one upon the other. These pots are then placed upon a thick bed of spent tan-

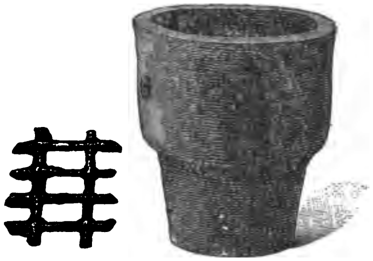

FIG. 152.

bark (in the original method, *dung*), upon the floor of a shed, and covered with planks. Upon these another layer of tan-bark is spread, and a second row of pots similarly charged. In this manner the layers of pots are built up to the roof of the shed, and the whole allowed to remain for about three months. Such a stack will contain many tons of lead, and about 65 gallons of dilute acetic acid to the ton of metal. The acid is gradually vaporised by the heat developed by the fermenting tan-bark, which results first in the formation of a basic lead acetate—

$$2H(C_2H_3O_2)+2Pb+O_2=Pb(C_2H_3O_2)_2,Pb(HO)_2.$$

This basic acetate is then acted upon by the carbon dioxide evolved during the fermentation, with the production of a mixture of normal lead acetate and basic lead carbonate, thus—

$$3\{Pb(C_2H_3O_2)_2,Pb(HO)_2\}+2CO_2=3Pb(C_2H_3O_2)_2+2PbCO_3,Pb(HO)_2+2H_2O.$$

And the lead acetate, in the presence of air and moisture, reacts upon a further portion of the metal, regenerating the basic acetate, which is once more decomposed by carbon dioxide—

$$Pb(C_2H_3O_2)_2+Pb+O+H_2O=\{Pb(C_2H_3O_2)_2,Pb(HO)_2\}.$$

In this cycle of reactions, therefore, the acetic acid acts as a carrier, a comparatively small quantity being able to convert an indefinite amount of lead into *white lead.*

White lead is also prepared by passing carbon dioxide into a solution of the basic acetate, obtained by boiling plumbic oxide (litharge) with lead acetate. The product, however, is not so opaque as that obtained by the former method, and is therefore not so valuable as a pigment. (This method is known as the *Clichy*, or Thénard's process.)

Milner's process consists in grinding together litharge, sodium chloride, and water, whereby a mixture of an oxychloride of lead and sodium hydroxide is formed—

$$4PbO+2NaCl+5H_2O=PbCl_2,3PbO,4H_2O+2NaHO,$$

and then passing carbon dioxide into the mixture, which converts it into *white lead* and sodium chloride, thus—

$$3[PbCl_2,3PbO,4H_2O]+6NaHO+8CO_2=6NaCl$$
$$+4[2PbCO_3,Pb(HO)_2]+11H_2O.$$

White lead is a heavy, amorphous powder, whose value as a pigment, or body colour, depends upon its opacity and density. Although this compound labours under the disadvantages of being extremely poisonous, and of becoming blackened by sulphuretted hydrogen, no substitute for it has yet been found which possesses the same "body" or covering power.

Lead Sulphate, $PbSO_4$.—The mineral *anglesite*, $PbSO_4$, occurs in the form of rhombic crystals, isomorphous with strontium and barium sulphates. Lead sulphate is obtained as a white powder, by precipitating a lead salt with sulphuric acid or a soluble sulphate. It is soluble in water only to an extremely slight extent, and still less in dilute sulphuric acid, but strong sulphuric acid dissolves it readily. It also dissolves in potassium hydroxide, and in many ammoniacal salts, notably the acetate, and in sodium thiosulphate.

An acid sulphate, of the composition $PbSO_4,H_2SO_4,H_2O$, is obtained by boiling the normal sulphate with sulphuric acid ; and a basic sulphate, $PbSO_4,PbO$, is formed by the action of ammonia upon the normal salt.

Lead Disulphate, $Pb(SO_4)_2$.—This substance is obtained by the electrolysis of sulphuric acid of sp. gr. 1.7 to 1.8 at a temperature not above 30°, employing an anode of lead. The cell is divided by a porous partition, and the compound collects as a muddy deposit in the anode compartment. Lead disulphate is a crystalline substance having a faint greenish colour. It is immediately decomposed by water into lead peroxide and sulphuric acid—

$$Pb(SO_4)_2+2H_2O=2H_2SO_4+PbO_2.$$

Sulphuric acid of a sp. gr. less than 1.65 decomposes it in a similar manner, but in concentrated sulphuric acid it is slightly soluble, 100 c.c. acid at 30° dissolving 0.345 gram of the compound. Concentrated hydrochloric acid and glacial acetic acid convert it respectively into lead tetrachloride, $PbCl_4$, and lead tetracetate, $Pb(C_2H_3O_2)_4$. Each of these compounds, like the disulphate, is decomposed by water into lead peroxide and the respective acid. Double salts, such as $K_2Pb(SO_4)_3$ and $(NH_4)_2Pb(SO_4)_3$, have been prepared, which are more stable than the disulphate itself.

Lead Sulphide, PbS.—The natural sulphide, *galena*, is found in the form of cubical crystals, possessing very much the colour and the metallic lustre of freshly cut lead. It is artificially formed when lead is heated in sulphur vapour, or when sulphuretted hydrogen is passed through a solution of a lead salt.

When heated in vacuo, or in a stream of an inert gas, lead sulphide melts, and sublimes in the form of small cubes. When heated with free access of air it is converted into lead sulphate.

Boiling dilute nitric acid converts lead sulphide into the nitrate, with separation of sulphur; but strong nitric acid oxidises it into lead sulphate. It is decomposed by hot concentrated hydrochloric acid, with evolution of sulphuretted hydrogen.

When sulphuretted hydrogen is passed into a solution of lead chloride, the precipitate which forms is first yellow, then reddish-brown, and finally black; the yellow and red precipitates are compounds of lead chloride and lead sulphide, termed sulphochlorides, having the composition, $PbS,PbCl_2$, and $3PbS,PbCl_2$.

The compounds of lead are powerful poisons, and when continuously taken into the system in small quantities, they act as cumulative poisons. Painters and others who constantly handle white lead are liable to suffer from chronic lead poisoning.

CHAPTER X

ELEMENTS OF GROUP V. (FAMILY A.)

Vanadium, $V = 51.2$; *Niobium*, $Nb = 94$; *Tantalum*, $Ta = 183$.

THE three rare metals comprising this family are closely related to each other, and also to the elements of family B of the same group, namely, the nitrogen and phosphorus series.

Vanadium occurs in a few rare minerals, as *vanadite*, $3Pb_3(VO_4)_2,PbCl_2$ (the vanadium analogue of pyromorphite); *pucherite*, $BiVO_4$; *mottramite*, $(PbCu)_3(VO_4)_2,2(PbCu)(HO)_2$. Small quantities also occur in certain iron ores, the vanadium ultimately finding its way into the Bessemer slag, in which it has been found concentrated to the extent of 1.5 per cent.

Metallic vanadium was first isolated by Roscoe (1867), although its existence was previously discovered by Del Rio (1801). The metal is extremely difficult to obtain, as at a red heat it combines with oxygen with great readiness, yielding the pentoxide V_2O_5, and also with nitrogen, forming the nitride VN. The element is prepared by heating the dichloride in a stream of perfectly pure hydrogen—

$$VCl_2 + H_2 = 2HCl + V.$$

Vanadium is unacted upon by air at ordinary temperatures, but when heated burns brilliantly to the pentoxide.

Niobium and tantalum are found associated together in the rare mineral *tantalite* or *columbite*. The first to be discovered was tantalum (Hatchett, 1801), and was originally named *columbium;* and the name niobium (from Niobe, the daughter of Tantalus) was given to the allied element by Rose (1846). Niobium is obtained by heating the trichloride, $NbCl_3$, in a stream of hydrogen.

Vanadium forms five oxides, corresponding to the oxides of nitrogen, while three oxides of niobium and two of tantalum are known :—

$$\begin{array}{ccccccccc} V_2O & ; & V_2O_2(\text{or } VO) & ; & V_2O_3 & ; & V_2O_4(\text{or } VO_2) & ; & V_2O_5. \\ — & ; & NbO & ; & — & ; & NbO_2 & ; & Nb_2O_5. \\ — & ; & — & ; & — & ; & TaO_2 & ; & Ta_2O_5. \end{array}$$

The pentoxides are obtained when the metals are burned in air or oxygen. They give rise respectively to vanadates, niobates, and tantalates, corresponding to nitrates and metaphosphates, thus—

Sodium nitrate, $NaNO_3$.
Sodium metaphosphate, $NaPO_3$.
Sodium metavanadate, $NaVO_3$.
Sodium metaniobate, $NaNbO_3$.
Sodium metatantalate, $NaTaO_3$.

The closer relation of these elements to phosphorus than to nitrogen is seen in the formation of salts derived from ortho- and pyro-acids, corresponding to orthophosphates and pyrophosphates. The naturally occurring vanadium compounds above mentioned are vanadates derived from the hypothetical orthovanadic acid, H_3VO_4. Both metavanadic acid, HVO_3, and pyrovanadic acid, $H_4V_2O_7$, have been obtained. Unlike the phosphorus compounds, the metavanadates are the most stable of the three classes of salts, and the orthovanadates the least stable. The most important of these salts is the ammonium metavanadate, NH_4VO_3, which is prepared by dissolving the pentoxide in ammonia. This salt is insoluble in ammonium chloride, and use is made of this property in the preparation of vanadium compounds from the mineral ***mottramite***. When ammonium metavanadate is ignited, vanadium pentoxide is obtained—

$$2NH_4VO_3 = V_2O_5 + 2NH_3 + H_2O.$$

Vanadium acts also as a feeble base. Thus, when the tetroxide, or hypovanadic oxide, is dissolved in sulphuric acid, hypovanadic sulphate, $V_2O_2(SO_4)_2$, is formed. The solution of this salt possesses a rich blue colour.

Vanadium forms three chlorides, having the composition—

$$VCl_2 \text{ (or } V_2Cl_4\text{)} ; \; VCl_3 \text{ (or } V_2Cl_6\text{)} ; \; VCl_4.$$

Niobium gives a trichloride, $NbCl_3$, and pentachloride, $NbCl_5$, while only the pentachloride of tantalum is known, $TaCl_5$.

Vanadium forms a number of compounds with oxygen and chlorine. Thus, when vanadium tetrachloride is acted upon by water, it yields hypovanadic chloride, $V_2O_4Cl_2$, which dissolves in the water, giving a blue solution.

Vanadium oxychloride, or vanadyl trichloride, $VOCl_3$, corresponds to phosphorus oxychloride, $POCl_3$. From vanadyl trichloride, by treatment with zinc, vanadyl dichloride is obtained, $VOCl_2$, and by the action of hydrogen at a high temperature upon this, both vanadyl monochloride, VOCl, and divanadyl-monochloride, V_3O_2Cl, are formed.

CHAPTER XI

ELEMENTS OF GROUP VI. (FAMILY A.)

Chromium, Cr	52.1	*Tungsten*, W	184
Molybdenum, Mo	96	*Uranium*, U	239.5

CHROMIUM.

Symbol, Cr. Atomic weight = 52.1.

Occurrence.—Chromium does not occur in nature in the uncombined state. In combination with oxygen and associated with iron it is met with in considerable quantities in the mineral *chrome iron ore*, or *chromite*, Cr_2O_3,FeO. This ore is the chief source of chromium compounds. Other natural compounds are *crocoisite*, $PbCrO_4$, and *chrome-ochre*, Cr_2O_3. Traces of chromium are present in various minerals, such as the emerald and green serpentine, and impart to them their green colour.

Modes of Formation.—Until quite recently metallic chromium was a mere chemical curiosity. It may be obtained by the reduction of the oxide, Cr_2O_3, by means of carbon at the high temperature of the electric furnace. The metal so produced, however, always contains carbon.

It is now produced on a manufacturing scale, by reducing the oxide by means of metallic aluminium. The powdered oxide mixed with the requisite quantity of powdered aluminium is placed in a refractory crucible, and the mixture ignited by means of a fuse.

The ignition temperature of this mixture being very high, the most suitable fuse for the purpose consists of a mixture of barium peroxide and powdered aluminium. A small quantity of this mixture is placed in a depression made in the surface of the charge in the crucible, and a piece of magnesium ribbon inserted into it. When the magnesium is ignited it immediately fires the fuse, which in its turn communicates its combustion to the charge. The contents of the crucible undergo rapid vivid combustion, and the temperature of the entire mass rises sufficiently high to melt the reduced chromium.

Properties.—Chromium is a hard, steel-grey metal, which is not oxidised in dry air. Its melting-point is about 2000°, being somewhat higher than that of platinum. The metal has no magnetic properties. It dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen. When placed in nitric acid chromium assumes the so-called *passive* condition, and while in this state it is unacted upon by the acids which dissolve it under normal conditions.

Metallic chromium when added to steel imparts to the latter a high degree of hardness and tenacity, and it is now largely employed in the production of these "chrome steels," which contain from 0.4 up to as much as 2 or 3 per cent. of chromium.

Oxides of Chromium.—Two oxides of chromium are definitely known, namely—

Chromium sesquioxide (*chromic oxide*) . .	Cr_2O_3.
Chromium trioxide (*chromic anhydride*) . .	CrO_3.

The first is a basic, and the second an acidic oxide. Besides these two compounds, a hydrated oxide, derived from the unknown chromous oxide, also exists, having the composition CrO,H_2O, or $Cr(HO)_2$. It is obtained as a yellowish precipitate by adding potassium hydroxide to a solution of chromium dichloride (chromous chloride), with the exclusion of air. It rapidly absorbs oxygen, turning dark brown. When heated out of contact with air it is converted into the sesquioxide, with evolution of hydrogen—

$$2CrO,H_2O = Cr_2O_3 + H_2O + H_2.$$

Other compounds of chromium and oxygen are described, whose composition, however, is not definitely established; thus, the product obtained as a brown powder, either by the partial reduction of the trioxide or the oxidation of the sesquioxide, is regarded by some chemists as chromium dioxide, CrO_2, and by others as chromium chromate, Cr_2O_3,CrO_3. It is readily obtained by passing nitric oxide into a solution of potassium dichromate.

Chromium Sesquioxide, Cr_2O_3, is obtained as a grey-green powder, when either the hydroxide, or the trioxide, or ammonium dichromate is ignited (see page 230).

When the vapour of chromyl dichloride, CrO_2Cl_2, is passed through a red-hot tube, chromic oxide is deposited in the form of dark-green hexagonal crystals. Chromic oxide which has been strongly ignited is nearly insoluble in acids. It is used under the name of *chrome green* as a pigment, and for giving a green colour to glass.

Chromic Hydroxides.—Chromic oxide yields a number of hydrated compounds. When ammonia is added to a solution of chromic chloride, or other chromic salt, free from alkali, a light blue compound is precipitated, which, when dried over sulphuric acid, has the composition $Cr_2(HO)_6,4H_2O$ (or $Cr_2O_3,7H_2O$). When this is dried in vacuo it loses $3H_2O$, and becomes $Cr_2(HO)_6, H_2O$ (or $Cr_2O_3,4H_2O$); and on being heated at 200°, it again parts with $3H_2O$, and has the composition Cr_2O_3,H_2O.

When potassium dichromate and boric acid are heated to dull redness, and the mass treated with water, a rich green residue is obtained, having the composition $Cr_2O_3,2H_2O$. This compound, known as *Guignet's green*, is employed as a pigment.

The first two of these compounds, which may be looked upon as consisting of the hydroxide $Cr_2(HO)_6$ in a hydrated condition, namely, $Cr_2(HO)_6,4H_2O$ and $Cr_2(HO)_6,H_2O$, are readily soluble in acids, yielding the chromic salts.

Chromium Trioxide (*chromic anhydride*) CrO_3.—When strong sulphuric acid is added to a cold saturated solution of potassium dichromate, the trioxide separates out in long, red, needle-shaped crystals—

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

The liquid is decanted from the crystals, which are drained upon porous tiles, and the adhering sulphuric acid and potassium sulphate washed away by strong nitric acid. The crystals are finally heated upon a sand-bath, whereby the nitric acid is evaporated.

Chromium trioxide dissolves in water to the extent of 62 parts in 100 parts of water at 26°. It melts at a temperature about 192°. At 250° it begins to give off oxygen, and is ultimately converted into the sesquioxide—

$$2CrO_3 = Cr_2O_3 + 3O.$$

Chromium trioxide is a powerful oxidising agent, and in contact with most organic substances it is reduced. In the preparation of the compound, therefore, the liquid cannot be filtered through paper in the usual way. Warm alcohol dropped upon the trioxide at once takes fire, while in a more diluted condition it is oxidised to acetic acid; and the reduction of the chromium trioxide is made evident by the change of colour of the liquid, from red or yellow to olive green.

Gaseous ammonia reduces the trioxide to the sesquioxide, with formation of water and nitrogen—

$$2NH_3 + 2CrO_3 = Cr_2O_3 + N_2 + 3H_2O,$$

the reaction being accompanied with the evolution of so much heat that the chromic oxide produced becomes incandescent.

When hydrogen peroxide is added to a dilute solution of chromium trioxide, or to a dilute solution of potassium dichromate, acidified with sulphuric acid, a deep indigo-blue solution is obtained. This blue compound is believed to contain *perchromic acid*, but its composition has not been definitely established. It may be regarded as a compound of chromium trioxide, CrO_3, or of perchromic acid, $HCrO_4$, with hydrogen peroxide, H_2O_2, in undetermined proportions.

In aqueous solution the blue colour quickly disappears, oxygen being eliminated. The compound is soluble in ether; and therefore, when the aqueous solution is shaken up with that liquid, a deep blue ethereal solution rises to the top. In this solution the compound is more stable, but when evaporated it evolves oxygen, leaving chromium trioxide. It is decomposed by alkalies, forming alkaline chromates with evolution of oxygen. The formation of this compound constitutes a delicate test for either chromium trioxide or hydrogen peroxide (see Hydrogen Peroxide, page 227).

Chromous Compounds.—These correspond to chromous hydrate, $Cr(HO)_2$, in which the chromium functions as a divalent element. Comparatively few of these salts are known.

Chromous Chloride, $CrCl_2$, is formed when the metal dissolves in hydrochloric acid. It is prepared in the anhydrous state by gently heating chromic chloride in a current of pure hydrogen. It is a white crystalline compound, soluble in water to a blue solution, which rapidly absorbs oxygen.

Chromous Sulphate, $CrSO_4,7H_2O$, is obtained by dissolving chromous acetate in dilute sulphuric acid. It is deposited from the solution in blue crystals, isomorphous with ferrous sulphate, $FeSO_4,7H_2O$.

Chromic Compounds.—These are derived from chromic oxide, the oxide acting as a base.

Chromic Chloride, $CrCl_3$, or Cr_2Cl_6, is prepared by strongly heating a mixture of chromic oxide, Cr_2O_3, and carbon in a stream of dry chlorine. The chromic chloride sublimes in the form of scales, having a reddish-pink colour. The molecular weight of chromic chloride is 158.45, showing that in the vaporous state its molecules have the formula $CrCl_3$.

It is nearly insoluble in water, but readily dissolves in water containing minute traces of chromous chloride, forming a green solution. The same solution is obtained by dissolving hydrated chromic hydroxide, $Cr_2(HO)_6,4H_2O$, in hydrochloric acid, and if this solution be slowly evaporated, very soluble green crystals separate out, having the composition $Cr_2Cl_6,12H_2O$. If strongly heated in the air, this compound gives off water and hydrochloric acid, leaving chromic oxide, Cr_2O_3; but when heated to 250°, in either gaseous hydrochloric acid or chlorine, it is converted into the pink anhydrous chromic chloride, which redissolves in water to the green solution. If heated strongly and sublimed, the compound obtained is nearly insoluble in water.

Chromic Sulphate, $Cr_2(SO_4)_3$, is obtained by dissolving chromium hydroxide in concentrated sulphuric acid, when a green solution is formed, which on standing changes to blue, and slowly deposits violet-blue crystals. The salt may be purified by dissolving in cold water and precipitating with alcohol. If insufficient alcohol be added to cause immediate precipitation, the salt slowly deposits from the dilute spirit in blue octahedrons, belonging to the regular system.

A cold aqueous solution, which has a violet colour, becomes green when boiled.

Chromic sulphate forms double salts with the sulphates of the alkalies, which belong to the alums.

Potassium Chromium Alum (*chrome alum*), $K_2SO_4,Cr_2(SO_4)_3,24H_2O$.—This double sulphate is formed when solutions of potassium and chromium sulphates are mixed together in molecular proportions. It is most conveniently prepared by the addition of the requisite amount of sulphuric acid to an aqueous solution of potassium dichromate, and reducing the chromic oxide by passing sulphur dioxide through the liquid—

$$(1)\quad K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + H_2O + K_2SO_4.$$
$$(2)\quad 2CrO_3 + 3SO_2 = Cr_2(SO_4)_3.$$

The resulting solution, containing the two sulphates in molecular proportions, deposits crystals of the double sulphate, in the form of dark plum-coloured octahedrons (Fig. 147, B, page 619), which appear red by transmitted light.

Chrome alum dissolves in water, yielding a plum-coloured solution, which on boiling turns green, but on long standing returns to its original colour.

Sodium chromium alum is more soluble, and ammonium chromium alum is less soluble, than the potassium salt.

Chromites.—Chromic oxide acts also as a weak acid, and combines with other oxides, forming compounds resembling the aluminates. When potassium hydroxide is added to a solution of a chromic salt, the green hydrated oxide which is precipitated contains alkali which cannot be removed by hot water; this is present in the form of potassium chromite. The best known chromites are zinc chromite, Cr_2O_3,ZnO; manganous chromite, Cr_2O_3,MnO, and ferrous chromite, Cr_2O_3,FeO; the latter occurs naturally as chrome iron ore.

Chromates.—When chromium trioxide is dissolved in water, the solution is believed to contain chromic acid, H_2CrO_4; when the solution is evaporated, however, the trioxide alone is left. (Red crystals have been obtained, by cooling a hot saturated solution of the trioxide, which have been regarded as the acid.)

Potassium Chromate, K_2CrO_4, is prepared by adding potassium hydroxide to a solution of the dichromate—

$$K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + H_2O.$$

On evaporation, the *yellow chromate of potash* separates out in rhombic crystals, isomorphous with potassium sulphate. It is soluble in water at the ordinary temperature to the extent of 60 parts in 100 parts of water, forming a yellow solution having an alkaline reaction.

Potassium Dichromate, $K_2Cr_2O_7$, is manufactured from chrome iron ore by roasting the finely crushed ore with potassium carbonate and lime in a reverberatory furnace; the mass being frequently raked over to expose fresh portions to the oxidising action of the flames. In this way a mixture of calcium and potassium chromates is produced—

$$2Cr_2O_3,FeO + 3K_2CO_3 + CaO + 7O = CaCrO_4 + 3K_2CrO_4 + Fe_2O_3 + 3CO_2.$$

The yellow mass, when cold, is broken up and lixiviated with a hot solution of potassium sulphate, which, by double decomposition with the calcium chromate, forms potassium chromate and precipitates calcium sulphate. The solution after settling is treated with the requisite quantity of sulphuric acid to convert the chromate into the dichromate, thus—

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

The dichromate being much less soluble than the normal chromate, a large proportion of it at once deposits as the solution cools; and the mother-liquor containing potassium sulphate is used again to lixiviate a fresh quantity of the roasted mixture.

Potassium dichromate forms large red prisms or tables, belonging to the asymmetric (triclinic) system. It is soluble in water at the ordinary temperature to the extent of 10 parts in 100 parts of water, yielding an acid solution, which is extremely poisonous. When a film of gelatine is impregnated with potassium dichromate and exposed to light, a reduction of the chromium to chromic oxide takes place, and at the same time the gelatine is rendered insoluble. This property is utilised in photographic processes.*

Potassium dichromate is also known under the misnomer *bichromate of potash*, which would suggest that the salt was in reality hydrogen potassium chromate, corresponding to bisulphate of potash, $HKSO_4$. Such a chromium compound does not exist. The dichromates correspond to the disulphates (or pyrosulphates), see page 435.

Potassium Trichromate, $K_2Cr_3O_{10}$ (or $K_2CrO_4,2CrO_3$), and **Potassium Tetrachromate**, $K_2Cr_4O_{13}$ (or $K_2CrO_4,3CrO_3$), are also known.

Lead Chromate, $PbCrO_4$, is found as the mineral *crocoisite*. It is produced by precipitation from a lead salt, with either potassium chromate or dichromate. It forms a bright yellow powder, known as *chrome-yellow*, and is employed as a pigment. It melts without decomposition, and resolidifies on cooling to a brown crystalline solid. At higher temperatures it gives off oxygen, and is converted into chromic oxide and a basic lead chromate. When heated with organic compounds, the latter are completely oxidised; lead chromate is therefore employed in organic analyses.

When lead chromate is digested with sodium hydroxide, or with normal potassium chromate, a basic lead chromate is obtained as a rich red powder—

$$2PbCrO_4 + 2NaHO = Na_2CrO_4 + H_2O + Pb_2CrO_5.$$

This compound is known as *chrome-red.*

Chromyl Chloride, CrO_2Cl_2.—This compound is prepared by distilling a mixture of potassium dichromate and sodium chloride with strong sulphuric acid. Chromyl chloride is a deep red, mobile, strongly fuming liquid. It is decomposed by water into hydrochloric acid and chromium trioxide, and acts as a powerful oxidising substance. When dropped upon phosphorus it explodes. When heated in sealed tubes it is converted into trichromyl chloride with loss of chlorine, $(CrO_2)_3Cl_2$.

Chromyl chloride may be regarded as being derived from

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* Abney, "Treatise on Photography."

chromic acid, $CrO_2(HO)_2$ (*unknown*), by the complete substitution of (HO) by Cl. The intermediate compound, chloro-chromic acid, $CrO_2(HO)Cl$, is also unknown, although its salts have been prepared; thus, by the gentle action of hydrochloric acid upon potassium dichromate, potassium chloro-chromate is obtained as a red crystalline salt—

$$K_2Cr_2O_7 + 2HCl = 2CrO_2(KO)Cl + H_2O.$$

Molybdenum, Mo=96; Tungsten, W=184; Uranium, U=238.5.

These three somewhat rare elements are closely related to chromium.

Molybdenum occurs in the mineral *molybdenite*, MoS_2 (which strongly resembles graphite in appearance), and more rarely as *molybdenum ochre*, MoO_3, and *wulfenite*, $PbMoO_4$.

Tungsten is found chiefly in *wolfram*, $2FeWO_4,3MnWO_4$ (occurring in the Cornish tin mines); more rarely as *scheelinite*, $PbWO_4$, and *wolfram ochre*, WO_3.

Uranium occurs as an oxide, $UO_2,2UO_3$, in *pitchblende* (a considerable quantity of which, associated with other uranium compounds, has recently been discovered at St. Stephens, Cornwall).

Molybdenum is obtained by the action of hydrogen upon the heated oxide or chloride; uranium, by the action of sodium upon the chloride; while tungsten has been obtained by both methods. In their specific gravities, tungsten and uranium exhibit a marked difference from chromium and molybdenum; thus, Cr, sp. gr.=6; Mo, sp. gr.=8.6; while W, sp. gr.=19.1; U, sp. gr.=18.7.

Molybdenum and uranium form a large number of oxides, some of which are regarded as definite oxides, while others are looked upon as combinations of two oxides. Only two oxides of tungsten are known. The composition of these compounds is as follows—

MoO	—	—	
Mo_2O_3	—	—	
MoO_2	WO_2	UO_2	$U_2O_5=UO_2,UO_3$.
MoO_3	WO_3	UO_3	$U_3O_8=UO_2,2UO_3$.
—	—	UO_4	

The trioxide of each metal is an acid oxide; uranium trioxide, however, is both acidic and basic. They are insoluble in water, but by the action of alkalies they yield molybdates, tungstates, and uranates. Molybdates and tungstates, derived from the acids $H_2MoO_4,2H_2O$ and $H_2WO_4,2H_2O$ (corresponding to chromic acid), are known. And all three oxides yield salts corresponding to potassium dichromate, thus—

Sodium Dimolybdate.	Sodium Ditungstate.	Sodium Diuranate.
$Na_2Mo_2O_7$	$Na_2W_2O_7$	$Na_2U_2O_7$.

Molybdic and tungstic acids also form numerous polymolybdates and polytungstates, by the absorption of varying quantities of the trioxide into the molecule of the normal salt (see Chromates, page 663). And in the case of tungsten, the compound metatungstic acid, $H_2W_4O_{13},7H_2O$, is known.

Uranium dioxide and trioxide are both basic oxides, the former yielding the unstable *uranous* salts, such as uranous sulphate, $U(SO_4)_2$; and the latter producing the *uranyl* salts, of which the sulphate, $(UO_2)SO_4$, and nitrate, $(UO_2)(NO_3)_2$, are well known.

Uranium peroxide, UO_4, is an acid oxide which yields per-uranates.

Both molybdic and tungstic acids form complex compounds with phosphoric acid, known as phospho-molybdic and phospho-tungstic acids: thus, when a nitric acid solution of ammonium molybdate $(NH_4)_2MoO_4$, is added in excess to a solution of orthophosphoric acid or an orthophosphate, a canary-yellow crystalline precipitate of ammonium phospho-molybdate, $2(NH_4)_3PO_4,22MoO_3,12H_2O$, is obtained (see page 477). It is soluble in alkalies and in excess of phosphoric acid, but insoluble in dilute mineral acids. When this compound is dissolved in *aqua-regia* the solution deposits yellow crystals of phospho-molybdic acid, $2H_3PO_4,22MoO_3$.

Compounds with chlorine having the following composition are known—

$MoCl_2$	WCl_2	—
$MoCl_3$ or Mo_2Cl_6	—	—
$MoCl_4$	WCl_4	UCl_4.
$MoCl_5$	WCl_5	UCl_5.
—	WCl_6	—

Manganese dioxide dissolves in cold concentrated hydrochloric acid, forming a dark-brown solution which is believed to contain the compound Mn_2Cl_6. On warming it evolves chlorine, and leaves manganous chloride, $MnCl_2$.

Manganites.—Manganese dioxide combines with certain metallic oxides, forming unstable compound oxides. Thus, with lime it forms CaO,MnO_2; $CaO,2MnO_2$, and $CaO,5MnO_2$. These compounds are produced in the *Weldon recovery process* (page 359).

MANGANOUS SALTS.

Manganous Chloride, $MnCl_2$, is the only chloride of this metal that has been isolated. It is obtained by dissolving any of the oxides or the carbonate in hydrochloric acid, and on evaporation is deposited as pink crystals of $MnCl_2,4H_2O$. The anhydrous salt is prepared by heating the crystals in a stream of hydrochloric acid. Manganese chloride forms double salts with chlorides of the alkalies, the ammonium salt $MnCl_2,2NH_4Cl,H_2O$ being the best known.

Manganous Sulphate, $MnSO_4$, is prepared by strongly heating a pasty mixture of the dioxide and strong sulphuric acid. The iron present is thereby converted into ferric oxide, and on treating the calcined mass with water manganous sulphate dissolves. The solution on evaporation deposits, at ordinary temperatures, large pink crystals of $MnSO_4,5H_2O$ (isomorphous with copper sulphate). Below 6° rhombic crystals are formed (also pink) of the composition $MnSO_4,7H_2O$ (isomorphous with ferrous sulphate).

When these salts are heated to 200°, or when their solutions are boiled, the anhydrous salt is formed. With sulphates of the alkalies, manganous sulphate forms double salts, as potassium manganous sulphate, $K_2SO_4,MnSO_4,6H_2O$; and with aluminium sulphate it yields a *pseudo-alum* (see page 620), $MnSO_4,Al_2(SO_4)_3,24H_2O$.

MANGANIC SALTS.

Manganic Chloride is obtained as a dark-brown solution when the dioxide is dissolved in cold hydrochloric acid. It has never been isolated, and is believed to have the composition Mn_2Cl_6.

Manganic Sulphate, $Mn_2(SO_4)_3$, is obtained as a green deliquescent powder by the action of sulphuric acid upon the precipitated peroxide. On exposure to the air the deliquesced mass becomes muddy, by the precipitation of hydrated manganic oxide, thus—

$$Mn_2(SO_4)_3+4H_2O=3H_2SO_4+Mn_2O_3,H_2O.$$

On the addition of potassium sulphate to a solution of manganic sulphate in dilute sulphuric acid, potassium manganese alum is obtained, $K_2SO_4,Mn_2(SO_4)_3,24H_2O$, which deposits in violet regular octahedra. In the presence of much water the salt is decomposed, and deposits the hydrated manganic oxide.

MANGANATES.

These salts are derived from the hypothetical manganic acid, H_2MnO_4. The oxide corresponding to this acid is known, viz., MnO_3. It is an unstable compound, obtained as a reddish amorphous mass, by adding a solution of potassium permanganate in sulphuric acid to dry sodium carbonate.

The manganates of the alkalies are obtained by fusing manganese dioxide with potassium or sodium hydroxide. If air be excluded the following reaction takes place—

$$3MnO_2+2KHO=K_2MnO_4+Mn_2O_3+H_2O.$$

In the presence of air or oxygen, or by the addition of potassium nitrate or chlorate, more of the manganese is converted into manganate. The fused mass has a dark-green colour, and dissolves in a small quantity of cold water. to a deep green solution, which is only stable in the presence of free alkali.

When a solution of potassium manganate is largely diluted or gently warmed, it changes from green to pink, owing to the conversion of the manganate into permanganate, thus—

$$3K_2MnO_4+2H_2O=2KMnO_4+MnO_2+4KHO.$$

The same change takes place when carbon dioxide is passed through the solution.

PERMANGANATES.

These salts are derived from permanganic acid, $HMnO_4$. When potassium permanganate is cautiously added to cold strong sulphuric acid, green oily drops of the unstable manganese heptoxide (or *permanganic anhydride*) are obtained, Mn_2O_7. This compound dissolves in a small quantity of water to a purple solution, which contains the unstable acid, Mn_2O_7,H_2O, or $H_2Mn_2O_8=2HMnO_4$. The solution evolves oxygen and deposits manganese dioxide.

Potassium Permanganate, $KMnO_4$, is the most important salt of this class. It is prepared by fusing the dioxide with potassium hydroxide and potassium chlorate, dissolving the manganate so obtained in water, and passing carbon dioxide through the solution. The filtered solution, on evaporation, deposits dark purple rhombic prisms, which appear deep red by transmitted light. Potassium permanganate is isomorphous with potassium perchlorate, $KClO_4$; it dissolves in water, forming a rich purple solution. When boiled with strong caustic alkalies it loses oxygen and forms the green potassium manganate—

$$2KMnO_4+2KHO=2K_2MnO_4+H_2O+O.$$

It readily gives up oxygen to oxidisable and organic compounds, and on this account is used both as a laboratory oxidising agent and as a disinfectant. The crude sodium salt is largely employed, under the name of *Condy's Disinfecting Fluid*, for this purpose. When solid potassium permanganate is heated to 240° it evolves oxygen, and forms potassium manganate and manganese dioxide—

$$2KMnO_4=K_2MnO_4+MnO_2+O_2.$$

CHAPTER XIII

THE TRANSITIONAL ELEMENTS OF THE FIRST LONG PERIOD

Iron, Fe=55.9.   Cobalt, Co=59.0.   Nickel, Ni=58.7.

THESE three elements belonging to Group VIII. (see classification, page 118) stand in a different relation to each other than the members of the other seven groups.

Iron, cobalt, and nickel belong to the same *period*, being the transitional elements falling between the first and second series of the first long period. They are related, on the one hand, through iron, to the preceding metals manganese and chromium (*see such compounds as ferrates*, *manganates*, *chromates*); while, on the other hand, through nickel, they approach the metal copper, which is the next following in the period.

Iron, cobalt, and nickel are closely related elements; in nature they are usually associated together. They are all attracted by the magnet, and are nearly white, hard, and difficultly fusible metals. In their chemical habits, however, they exhibit a gradual transition in their properties. Thus, iron forms two basic oxides, yielding two series of stable salts, viz., *ferrous* and *ferric*. Cobalt also has two basic oxides, but the basicity of the sesquioxide is very feeble, and cobalt*ic* salts (except double salts) are unstable, and are only known in solution. Nickel only forms one basic oxide, and yields only one series of salts corresponding to the ferrous salts, the sesquioxide of nickel behaving with acids as a peroxide.

IRON.

Symbol, Fe.   Atomic weight=55.9.

Occurrence.—Iron is one of the most abundant and widely distributed elements. It occurs in the uncombined state in small particles disseminated through certain basalts, and also in meteoric iron, where it is usually associated with nickel, cobalt, and copper. Masses of iron have also been found which have been formed by the reduction of iron ores, owing to the firing of coal pits: such iron is known as *natural steel.*

The chief ores of iron are *red hæmatite* and *specular iron ore*, Fe_2O_3; *brown hæmatite*, $2Fe_2O_3,3H_2O$; *magnetic iron ore* (loadstone), Fe_3O_4; *spathic iron ore*, $FeCO_3$; *clay iron stone* consists of spathose iron mixed with clay; and *blackband* is clay iron stone containing from 20 to 25 per cent. of coal.

Iron is also found in combination with sulphur, as *iron pyrites*, FeS_2, and with iron and copper in copper pyrites, Cu_2S,Fe_2S_3, but these compounds are not employed in the metallurgy of iron.

Modes of Formation.—Iron is readily reduced from its compounds. Thus, if ferric oxide or oxalate be gently heated in a stream of hydrogen, the metal is obtained as a black powder, which spontaneously oxidises with incandescence when brought into the air. On the industrial scale the reduction is effected by means of coke and limestone. The ore is first calcined, whereby water and carbon dioxide are expelled, and any sulphides present are oxidised, with the expulsion of sulphur dioxide. By this process also the ore is rendered more porous. The calcined ore is then smelted in a blast-furnace, with limestone and coke. Fig. 153 shows in section a modern blast-furnace. The charge is admitted at the top by means of the cup and cone arrangement, which closes the furnace, and a powerful hot-blast is forced through tuyeres placed round the base of the furnace. The furnace gases are led off by the side pipe at the top, and are utilised for heating the blast.

The chemical reactions which take place in a blast-furnace are many and complex, and differ in different parts of the furnace. In the main, the following are the changes which occur. The atmospheric oxygen of the hot-blast, on coming in contact with the carbon, forms carbon monoxide (at the high temperature carbon dioxide is probably not first formed). As the charges of ore gradually work their way down the furnace, they soon arrive at a point where the ferric oxide begins to be reduced by the heated carbon monoxide, first to ferrous oxide, and then to a spongy or porous mass of metallic iron. The region where this takes place is termed the *zone of reduction*—

$$Fe_2O_3 + 3CO = 3CO_2 + 2Fe.$$

In the early stages of its descent through the furnace, the limestone is converted into carbon dioxide and lime. The reduced spongy metal, as it passes down through the hotter regions of the furnace, begins to take up carbon. It is probable that carbon monoxide first combines with the reduced iron, forming iron carbonyl (see page 300), which at a higher temperature is decomposed, with the precipitation of finely divided carbon within the pores of the mass. More and more carbon is taken up by the iron

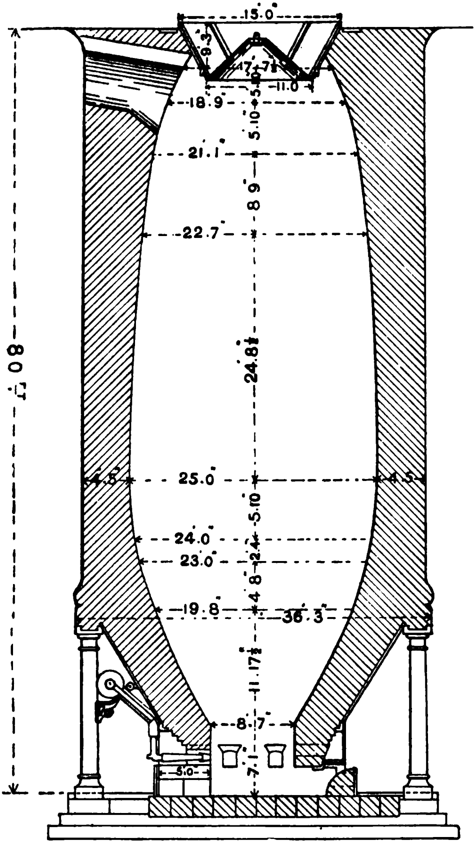

FIG. 153.

as it descends, until it passes from a pasty condition to a state of complete fusion, when it collects upon the bottom, or hearth, of the furnace. In passing through the hottest regions the lime combines with the siliceous materials originally present in the ore to form a fusible slag, beneath which the molten iron collects. Other reactions which go on in various regions of the furnace are the reduction of sulphur compounds, and of phosphates and silicates, with the absorption into the iron of a certain amount of sulphur, phosphorus, and silicon. The precise nature of the changes suffered by the gases in the various regions of the furnace is still obscure. The cyanogen formed by the direct union of atmospheric nitrogen with carbon, and also the hydrocarbons present, doubtless undergo a chemical change in contact with the heated iron, and probably aid in its carburisation. The molten iron is drawn off at intervals from a tap-hole into moulds, and is known as *cast iron* or *pig iron*. The slag as it accumulates overflows in a regular stream through an opening known as the *slag hole*. When such a furnace is in full blast, fresh charges of materials are introduced at regular intervals, and the process continues uninterruptedly for years. The metal obtained from the blast-furnace is far from pure iron, but contains varying quantities of carbon, silicon, phosphorus, sulphur, and manganese.

The carbon may be present either in combination with iron as a carbide, or distributed throughout the metal as fine particles of graphite, or in both of these forms. *White cast iron* contains its carbon in the combined form, while *grey cast iron* owes its grey colour to the presence of minute crystals of graphite disseminated throughout the metal. When grey cast iron is dissolved in hydrochloric acid, the graphite remains behind as a black powder; but on similarly treating iron containing *combined carbon*, the carbon unites with the hydrogen, forming various hydrocarbons, which impart to the escaping gas a characteristic and unpleasant smell. Average cast iron contains from 90 to 95 per cent. of iron, and 3 to 5 per cent. of carbon. *Spiegel* is a variety of white cast iron containing 3.5 to 6 per cent. of carbon, and from 5 to 20 per cent. of manganese. With more than 20 per cent. of manganese, the metal is termed *ferro-manganese*.

Purification.—The properties of iron are greatly modified by the presence of various impurities, especially carbon, and for different purposes for which iron is used, metal of different degrees of purity is required. The purest form of ordinary commercial iron is known as *wrought iron*, while *steel* is intermediate between this and *cast iron.*

The process by which cast iron is converted into wrought iron is termed *puddling;* and the method is called either *dry* puddling or *pig-boiling*, depending upon whether the cast iron is subjected to a preliminary refining or not. The chemical reactions in both cases are the same, and consist in the oxidation of the impurities; the carbon being expelled as carbon dioxide, while the oxides of silicon, phosphorus, and manganese pass into the slag. The method of *pig-boiling* is almost exclusively adopted.

The cast iron is melted in a reverberatory furnace, the working bottom of which, as well as the lining (or *fettling*), consists of a layer of ferric oxide. The decarburisation of the iron is mainly effected by means of the oxide of iron derived from the fettling; and for some time the molten mass appears to boil, owing to the escape of carbon monoxide. As the impurities are oxidised and removed, the mass becomes pasty (owing to the fact that the melting-point of pure iron is much higher than that of cast iron), and is then worked up into lumps, or *blooms*, which are ultimately removed and placed under a steam hammer, whereby admixed slag is squeezed out, and the metal is welded into a solid mass.

Wrought iron contains from 0.06 to 0.15 per cent. of carbon.

Steel may be produced either from wrought iron, by adding carbon, or from cast iron by removing that impurity. Formerly steel was exclusively obtained by the first method, by what is known as the *cementation process.* This simply consists in heating the bars of iron, buried in broken charcoal, for several days to a red heat. The precise nature of the chemical change which results in the carburisation of the iron is not definitely established. In all probability the carbon is conveyed into the body of the metal (which is not even heated to the softening point) by the intervention of iron carbonyl; the carbon monoxide being formed by the union of the carbon with the air retained within the layer of charcoal. At the conclusion of the operation the iron presents a blistered appearance, and on this account is termed *blister-steel.*

At the present time steel is mostly produced by the *Bessemer process*, which consists in oxidising the impurities present in cast iron, by blowing through the molten metal a blast of air. This operation is performed in a large pear-shaped vessel, known as a *converter*, which is mounted on trunnions, and through the bottom of which a powerful air blast can be admitted. The converter is tilted into a horizontal position, and a quantity of molten cast iron is run in. The air blast is then started and the converter immediately swung back into a vertical position. In the course of a very short time the whole of the impurities are burnt away, and the stage at which the operation is complete is sharply marked, by the sudden disappearance of the flame from the open mouth of the converter. The converter is once more swung into a horizontal position, and the blast is stopped. The exact quantity of molten spiegel is then added to supply the carbon required to convert the entire charge into steel, and the blast is turned on for a few moments in order to thoroughly mix the materials, after which the contents are poured out into the casting ladle.

The comparative purity of the three forms of iron will be seen from the three following typical examples :—

	Cast Iron.	Steel.	Wrought Iron.
Carbon	3.81	0.65	0.10
Silicon	1.68	0.07	0.05
Phosphorus	0.70	0.03	0.15
Sulphur	0.60	0.02	0.05
Manganese	0.41	0.40	0.07
	7.20	1.17	0.42
Iron	92.80	98.83	99.58
	100.00	100.00	100.00

Properties.—Pure iron is a white lustrous metal, capable of taking a high polish. Its specific gravity is 7.84 to 8.139. It is more difficultly fusible and more malleable than wrought iron, but at a red heat it becomes soft and can be welded. The physical properties usually associated with iron are in reality those of iron containing varying amounts of impurities: thus, pure iron when rendered magnetic quickly loses this property, whereas steel retains its magnetism at ordinary temperatures, losing it, however, when heated. Pure iron, when heated and suddenly cooled, does not take a *temper*, while steel when so treated becomes extremely hard and brittle.

Iron is unacted upon by dry air at ordinary temperatures, but in moist air, especially in the presence of carbon dioxide, it becomes coated with rust, and the process, which is slow to begin, proceeds rapidly when a film of oxide has been once formed. Iron decomposes water readily at a red heat; in the finely divided state the metal decomposes water at 100°. Dilute hydrochloric and sulphuric acids rapidly dissolve iron with evolution of hydrogen. Dilute nitric acid dissolves it, forming ferrous nitrate and ammonium nitrate; with stronger nitric acid, ferric nitrate and oxides of nitrogen are formed.

Concentrated nitric acid (specific gravity, 1.45) is without solvent action upon iron. A strip of iron which has been immersed in such strong acid is unacted upon when afterwards dipped into the more dilute acid, and is also incapable of precipitating metallic copper from a solution of copper sulphate. Iron in this condition is said to be *passive*. Other oxidising agents, as chromic acid, or hydrogen peroxide, are capable of bringing about the same result. It is believed that this condition is due to the formation of a film of the oxide Fe_3O_4 upon the surface.

Finely divided iron takes fire spontaneously in chlorine; and when gently warmed in sulphur dioxide it combines with that gas with incandescence. It absorbs carbon monoxide with formation of iron carbonyl, $Fe(CO)_5$. When heated in ammonia it forms a nitride, Fe_4N_2 (see page 278).

Oxides of Iron.—Three oxides of iron are known, namely :—

Ferrous oxide (*iron monoxide*)	FeO.
Ferric oxide (*iron sesquioxide*)	Fe_2O_3.
Ferroso-ferric oxide (*magnetic oxide*)	Fe_3O_4, or Fe_2O_3,FeO.

The two first are basic oxides, giving rise respectively to ferrous and ferric salts; the third yields both ferrous and ferric salts.

Ferric oxide combines with certain more basic oxides, forming compounds analogous to Fe_2O_3,FeO; such as Fe_2O_3,CaO, Fe_2O_3,ZnO. These are known as *ferrites*.

Ferrous Oxide (*protoxide of iron*), FeO, is formed as an intermediate product during the reduction of ferric oxide by hydrogen or carbon monoxide; but it is difficult to obtain it free from either the higher oxide or the metal. It is also formed when ferrous oxalate is heated out of contact with air. It is a black powder, which oxidises in the air, and which dissolves in acids yielding ferrous salts.

Ferrous Hydroxide, $Fe(HO)_2$, or FeO,H_2O, is obtained as a white precipitate when potassium hydroxide is added to a solution of a ferrous salt with entire exclusion of air. In the presence of air it is green. It readily absorbs oxygen and passes into ferric oxide.

Ferric Oxide (*sesquioxide of iron*), Fe_2O_3, occurs in brilliant black crystals belonging to the hexagonal system, in *specular iron ore.* It is obtained as a red amorphous powder by heating hydrated ferric oxide, ferrous sulphate, or ferrous carbonate. In a crystalline condition it may be produced by carefully heating a mixture of ferrous sulphate and common salt, or by heating the amorphous oxide in gaseous hydrochloric acid. The natural compound, and also the artificial substance after strong ignition, is only slowly dissolved by acids. Ferric oxide is extremely hygroscopic. When strongly heated it is partially converted into Fe_3O_4. The amorphous substance, obtained by distilling ferrous sulphate for the manufacture of Nordhausen sulphuric acid, is employed as a red pigment and a polishing powder under the name of *rouge.*

Ferric Hydroxide, or Hydrated Ferric Oxide, $Fe_2(HO)_6$, or $Fe_2O_3,3H_2O$.—When an excess of ammonia is added to a solution of ferric chloride, and the voluminous brown precipitate is dried at a moderate temperature, it has the composition $Fe_2O_3,3H_2O$. On exposure to various temperatures, or by precipitation under various conditions, hydrated oxides of the composition $Fe_2O_3, 2H_2O$; Fe_2O_3,H_2O, and others, have been obtained ; and several of these compounds occur in nature. Ordinary rust of iron has the composition $2Fe_2O_3,3H_2O$, or $Fe_2O_3,Fe_2(HO)_6$.

The monohydrate Fe_2O_3,H_2O has been obtained as a soluble modification, by heating an acetic acid solution of precipitated ferric hydroxide to 100° in sealed vessels. On the addition of sulphuric acid, a brown precipitate is obtained, having the composition Fe_2O_3,H_2O, which is insoluble in acids, but soluble in water. The solution gives no reaction with potassium ferrocyanide. Another soluble hydroxide is produced by dissolving the ordinary precipitated hydroxide in ferric chloride, and subjecting the solution to dialysis. This solution is employed in medicine under the name of *dialysed iron.*

Ferroso-ferric Oxide, Fe_3O_4, occurs native as *magnetite* and *magnetic oxide of iron;* the magnetic variety being known also as *loadstone.* When iron is heated in the air, the black film which forms (the so-called *iron-scale* or *hammer-scale*) consists of the oxide Fe_3O_4, with more or less ferric oxide, Fe_2O_3, upon the outer surface. It is also produced when steam or carbon dioxide is passed over heated iron, with evolution of hydrogen and carbon monoxide respectively, these reactions being the reverse of those by which oxides of iron are reduced by hydrogen or carbon monoxide.

This oxide is also formed as a black precipitate when ammonia is added to a solution containing mixed ferrous and ferric salts, and the mixture gently warmed.

Ferrates.—These compounds correspond to the manganates, but neither the acid H_2FeO_4 nor the oxide FeO_3 are known. Potassium ferrate, K_2FeO_4, is formed when chlorine is passed through a solution of potassium hydroxide in which ferric hydroxide is suspended.

FERROUS SALTS.

Ferrous Chloride, $FeCl_2$.—The anhydrous compound is obtained by heating iron wire in gaseous hydrochloric acid, when the salt sublimes in the form of white deliquescent crystals. In aqueous solution it is obtained when iron is dissolved in hydrochloric acid, and is deposited in pale blue-green crystals of $FeCl_2,4H_2O$.

When heated in the air it is converted into ferric oxide and chloride, the latter volatilising—

$$6FeCl_2 + 3O = Fe_2O_3 + 2FeCl_3.$$

When volatilised in an atmosphere of hydrochloric acid its vapour-density at high temperatures corresponds to the formula $FeCl_2$; at lower temperatures it lies between the values required for $FeCl_2$ and Fe_2Cl_4.

When strongly heated in a current of steam it is decomposed as follows—

$$3FeCl_2 + 4H_2O = Fe_3O_4 + H_2 + 6HCl.$$

Ferrous Sulphate (*green vitriol*), $FeSO_4,7H_2O$, is obtained when iron is dissolved in sulphuric acid. It is prepared on a large scale by exposing heaps of iron pyrites, FeS_2, to the action of air and moisture. The liquor which drains away contains ferrous sulphate and sulphuric acid, and the latter is converted into ferrous sulphate by the introduction of scrap iron.

Ferrous sulphate forms pale green monosymmetric crystals, which effloresce on exposure to the air. They are soluble in water to the extent of 70 parts in 100 parts of water at 15°, and 370 parts in 100 parts at 90°. At 100° the crystals lose $6H_2O$, being converted into $FeSO_4,H_2O$.

If a crystal of zinc sulphate be thrown into a supersaturated solution of ferrous sulphate, the iron salt is deposited in rhombic prisms (isomorphous with zinc sulphate). On the other hand, if a crystal of copper sulphate be added, asymmetric (triclinic) crystals of $FeSO_4,5H_2O$ (isomorphous with copper sulphate) are formed.

Ferrous sulphate forms double salts with the sulphates of the alkalies. Thus, when mixed with ammonium sulphate in the requisite proportions, ammonium ferrous sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, is obtained. This salt is less readily oxidised on exposure to air than ferrous sulphate itself.

Ferrous salts give, with potassium ferrocyanide ($K_4Fe(CN)_6$, or $4KCN,Fe(CN)_2$), a white precipitate of potassium ferrous ferrocyanide ($FeK_2Fe(CN)_6$, or $2KCN,2Fe(CN)_2$). The precipitate is quickly oxidised, and becomes blue. With potassium ferricyanide ($K_3Fe(CN)_6$, or $3KCN,Fe(CN)_3$), ferrous salts yield a blue precipitate of ferrous ferricyanide (*Turnbull's blue*) ($Fe_3\{Fe(CN)_6\}_2$, or $3Fe(CN)_2,2Fe(CN)_3$), thus—

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3\{Fe(CN)_6\}_2 + 3K_2SO_4.$$

FERRIC SALTS.

Ferric Chloride, $FeCl_3$, is prepared in the anhydrous state by passing dry chlorine over heated iron wire. In solution it may be obtained by dissolving iron in *aqua regia;* or ferric oxide in hydrochloric acid. The anhydrous salt forms nearly black crystals, appearing deep red by transmitted light. It readily volatilises, and at temperatures above 700° the density of its vapour corresponds to the formula $FeCl_3$, while at lower temperatures its density agrees more nearly with the formula Fe_2Cl_6.

Ferric chloride is extremely deliquescent, and readily dissolves in water. When the solution is slowly evaporated, yellow crystals are deposited, having the composition $Fe_2Cl_6,12H_2O$ (or $FeCl_3,6H_2O$). When a dilute solution of ferric chloride is boiled, it decomposes, forming either an insoluble oxychloride or a soluble hydroxide and free hydrochloric acid (depending upon the strength of the solution).

Ferric Sulphate, $Fe_2(SO_4)_3$, is prepared by the addition of sulphuric or nitric acids to a solution of ferrous sulphate—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 2NO + 4H_2O + 3Fe_2(SO_4)_3.$$

The brown solution, on evaporation, leaves the anhydrous salt as a white mass. When the requisite quantity of potassium sulphate is dissolved in a strong solution of ferric sulphate at 0°, the double potassium iron sulphate (iron alum), $K_2SO_4,Fe_2(SO_4)_3,24H_2O$, separates out in the form of violet octahedrons.

Ferric salts give, with potassium ferrocyanide ($K_4Fe(CN)_6$, or $4KCN,Fe(CN)_2$), a dark blue precipitate of ferric ferrocyanide (*Prussian blue*), $4Fe(CN)_3,3Fe(CN)_2$) or $Fe_4\{Fe(CN)_6\}_3$—

$$4FeCl_3+3K_4Fe(CN)_6=Fe_4\{Fe(CN)_6\}_3+12KCl.$$

With potassium ferricyanide ferric salts give no precipitate.

SULPHIDES OF IRON.

Ferrous Sulphide, FeS.—When a white-hot bar of wrought iron is dipped into melted sulphur, the elements unite; and the readily fusible monosulphide of iron falls to the bottom. It may be prepared by throwing into a red-hot crucible a mixture of iron filings and sulphur. So obtained, it is a dark, yellowish-grey, metallic-looking mass. When heated out of contact with air, it does not part with sulphur, but in the presence of air is converted into ferric oxide and sulphur dioxide. Ferrous sulphide is precipitated from either ferrous or ferric solutions, by alkaline sulphides, as a black amorphous powder, which in the moist state is quickly oxidised by the air. Dilute sulphuric acid, or hydrochloric acid, decomposes ferrous sulphide, with evolution of sulphuretted hydrogen.

Iron Sesquisulphide, Fe_2S_3, is formed when equal weights of iron and sulphur are heated to a moderate temperature. It cannot be obtained by precipitation from a ferric salt, as the product so formed consists of ferrous sulphide and sulphur—

$$Fe_2Cl_6+3(NH_4)_2S=6NH_4Cl+2FeS+S.$$

It is a yellow, metallic-looking solid, which is decomposed by dilute hydrochloric acid, yielding sulphuretted hydrogen.

Ferric Disulphide, FeS_2, occurs in nature in large quantities as *iron pyrites*, sometimes in the massive condition, and at others in the form of brass-yellow cubical crystals. In many cases the native compound bears the impression, or assumes the shape, of various organised forms, such as wood, ammonites, &c., the mineral having been formed by the reducing action of the organic matter upon ferrous sulphate in solution. Ferric disulphide is also found in the form of brass-like, rhombic crystals in *radiated pyrites.*

The compound may be prepared by heating to a low red heat a mixture of ferrous sulphide and sulphur.

Ferric disulphide is unacted upon by dilute acids: hot concentrated hydrochloric acid decomposes it, with liberation of sulphur and sulphuretted hydrogen. When heated in hydrogen, sulphur is evolved (which partly combines with the hydrogen), and ferrous sulphide remains. When heated in the air, ferric oxide and sulphur dioxide are formed.

Ferroso-ferric Sulphide (*magnetic pyrites*), Fe_3S_4, occurs in the form of hexagonal crystals. Like the corresponding oxide, this compound is attracted by the magnet, and is itself sometimes magnetic.

COBALT.

Symbol, Co. Atomic weight=59.0.

Occurrence.—Cobalt is not found uncombined in nature. Its chief natural compounds, which are only sparsely distributed, are *speiss-cobalt*, or *smaltine*, $CoAs_2$; *cobalt glance*, CoAsS, in both of which the cobalt is partially replaced by nickel and iron; and *cobalt-bloom*, $Co_3(AsO_4)_2,8H_2O$.

Modes of Formation.—Cobalt is obtained by reducing the oxide, or the chloride, in a stream of hydrogen, or by strongly heating cobalt oxalate in a closed crucible. It is also readily obtained by reduction of its oxide with powdered aluminium.

Properties.—Cobalt is an almost white, hard metal, which, when polished, resembles nickel, but is slightly bluer. It is malleable, and when heated is very ductile. Like both iron and nickel, it is attracted by the magnet; but unlike these, it retains this property, even at a red heat. In the massive form, cobalt is unacted upon by the air; but the finely-powdered metal, obtained by the reduction of the oxide in hydrogen, rapidly oxidises on exposure to the air, sometimes with incandescence. When heated in the air, it forms the oxide Co_3O_4. Cobalt decomposes steam at a red heat, yielding cobaltous oxide, CoO.

Oxides of Cobalt.—Three oxides of cobalt are recognised, namely, cobaltous oxide, CoO; cobaltic oxide, Co_2O_3; and cobalto-cobaltic oxide, Co_3O_4.

Four other oxides are known, which are regarded as compounds of the two first, having the composition $2CoO,Co_2O_3$; $3CoO,Co_2O_3$; $4CoO,Co_2O_3$: $6CoO,Co_2O_3$.

The monoxide, CoO, is basic, and yields the cobaltous salts. The sesquioxide, Co_2O_3, is feebly basic, forming only unstable salts. Stable double salts, however, corresponding to this oxide are known.

Cobaltous Oxide (*cobalt monoxide*), CoO, is formed when the sesquioxide is heated to redness in a stream of carbon dioxide, or gently heated in hydrogen. It is also obtained when the carbonate or hydroxide is heated in the absence of air. It forms a drab-coloured powder, which is unacted upon by the air, but when heated, forms Co_3O_4. When heated in either hydrogen or carbon monoxide, it is reduced to metallic cobalt.

Cobaltous Hydroxide, $Co(HO)_2$.—When potassium hydroxide is added to a solution of a cobaltous salt, a blue basic hydrate is precipitated, which, on boiling, is converted into the pink hydroxide $Co(HO)_2$. It turns brown on exposure to the air, by the absorption of oxygen. Both the oxide and hydroxide are really soluble in acids, giving cobaltous salts.

Cobaltic Oxide (*cobalt sesquioxide*), Co_2O_3, is obtained by carefully heating cobaltous nitrate until red fumes cease to be evolved. It is a dark grey powder, which, when strongly heated, is converted into the intermediate black oxide, Co_3O_4. Cobaltic oxide dissolves in cold acids, forming brown solutions, which contain unstable cobaltic salts. When warmed, these are converted into cobaltous salts, with evolution of oxygen in the case of oxy-salts, and of the halogen from haloid salts. This sesquioxide, therefore, behaves as a peroxide.

Cobaltic Hydroxide, $Co_2(HO)_6$, or $Co_2O_3,3H_2O$, is obtained as a nearly black precipitate, by the addition of an alkaline hypochlorite to a cobaltous salt. With acids it behaves as the oxide.

Cobalto-Cobaltic Oxide, Co_3O_4, is formed as a black powder, when the sesquioxide is strongly heated in air.

COBALTOUS SALTS.

Cobaltous Chloride, $CoCl_2$.—When the carbonate, or any of the oxides, are dissolved in hydrochloric acid, the concentrated solution deposits dark red prisms (monosymmetric), having the composition $CoCl_2,6H_2O$. When exposed over sulphuric acid, they lose $4H_2O$, and are converted into a rose-red salt, $CoCl_2,2H_2O$, which reabsorbs moisture from the air to form the hexahydrate.

When the dihydrate is heated to about 100°, it is converted into violet-blue crystals of $CoCl_2,H_2O$; and at 120° it becomes anhydrous, and is blue. The blue salts, on exposure to the air, rapidly rehydrate themselves, and become pink.

Cobaltous chloride dissolves in alcohol, giving a deep blue solution, which, on the addition of water, also becomes pink. This property of forming pink hydrated salts, which become blue or green when nearly or quite anhydrous, is common to most cobaltous salts. Thus, the iodide $CoI_2,6H_2O$ forms rose-coloured crystals. When gently heated, it changes to a moss-green salt, $CoI_2,2H_2O$, which, when dehydrated, becomes nearly black.

Cobaltous Sulphate, $CoSO_4,7H_2O$, is obtained by dissolving the carbonate or oxides in sulphuric acid, and is deposited from the solution in dark red crystals, isomorphous with ferrous sulphate. Cobalt sulphate, like the sulphates of iron and nickel, forms double salts with alkaline sulphates, of which cobalt potassium sulphate, $CoSO_4,K_2SO_4,6H_2O$, is the best known.

Cobaltic Salts.—Single salts corresponding to cobalt sesquioxide are unstable, and exist only in solution. More stable double salts are known. Thus, when potassium nitrite is added to an acetic acid solution of cobalt chloride, a yellow crystalline precipitate is obtained, consisting of the double nitrite of cobalt and potassium—

$$2CoCl_2 + 10KNO_2 + 4HNO_2 = Co_2(NO_2)_6,6KNO_2 + 2NO + 4KCl + 2H_2O.$$

The formation of this compound is made use of for separating cobalt from nickel, the latter element yielding no corresponding double nitrite. In the presence, however, of salts of barium, strontium, or calcium, nickel forms, with potassium nitrite, *triple* salts, such as $Ni(NO_2)_2,Ba(NO_2)_2,2KNO_2$, which are precipitated as yellow crystalline powders. Hence, in the presence of metals of the alkaline earths, nickel and cobalt cannot be separated by this method.

SULPHIDES OF COBALT.

Cobaltous Sulphide, CoS, is obtained by heating cobaltous oxide with sulphur, or by fusing a mixture of cobalt sulphate, barium sulphide, and common salt. It forms bronze-coloured crystals, which are soluble in strong hydrochloric acid. Cobalt sulphide is precipitated as a black amorphous powder when ammonium sulphide is added to a cobalt solution. The precipitate slowly dissolves in dilute mineral acids, but is insoluble in acetic acid. When heated in a stream of sulphuretted hydrogen, it yields the sesquisulphide Co_2S_3; and if mixed with sulphur, and heated in a current of hydrogen, it forms the disulphide CoS_2.

Cobaltamines (*ammoniacal cobalt compounds* *). Cobalt forms a large number of complex ammoniacal salts. A few of these contain the metal in the divalent condition, and are known as *ammonio-cobaltous salts;* but by far the larger number contain the hexavalent double atom Co_2, and are termed *ammonio-cobaltic compounds.* These compounds are classified as follows † :—

Ammonio-Cobaltous Salts are formed by the absorption of gaseous ammonia by anhydrous cobaltous salts, or by dissolving the salts in strong aqueous ammonia, with exclusion of air. In this way the following salts have been obtained—

Ammonio-cobaltous chloride, $CoCl_2,6NH_3$ which, at 120°, is converted into $CoCl_2,2NH_3$.
Ammonio-cobaltous sulphate, $CoSO_4,6NH_3$.
Ammonio-cobaltous nitrate, $Co(NO_3)_2,6NH_3,2H_2O$.

Ammonio-Cobaltic Salts.—These may be arranged under the following classes and subdivisions :—

I. *Hexammonio Salts.*—General formula, $Co_2(NH_3)_6 \cdot R_6$, where R equals a monacid radical, or its equivalent of *di* or *tri* acid radicals.

Examples
Hexammonio-cobaltic chloride (*dichro-cobaltic chloride*) $Co_2 \cdot (NH_3)_6 \cdot Cl_6,2H_2O$.
Hexammonio-cobaltic sulphate, $Co_2 \cdot (NH_3)_6 \cdot (SO_4)_3,6H_2O$.

II. *Octammonio Salts*—

(α.) *Praseo* ‡ *Salts.*—General formula, $Co_2 \cdot (NH_3)_8 \cdot R_6$.

Examples
Praseo-cobaltic chloride, $Co_2(NH_3)_8 \cdot Cl_6,2H_2O$.
Praseo-cobaltic chloro-nitrate, $Co_2(NH_3)_8 \cdot Cl_4 \cdot (NO_3)_2,2H_2O$.

(β.) *Fusco Salts.*—General formula, $Co_2(NH_3)_8(HO)_2 \cdot R_4$.

Examples
Fusco-cobaltic chloride, $Co_2(NH_3)_8(HO)_2 \cdot Cl_4,2H_2O$.
Fusco-cobaltic sulphate, $Co_2(NH_3)_8(HO)_2 \cdot (SO_4)_2,2H_2O$.

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* For details respecting the preparation and properties of these salts the student is referred to larger works.

† On the constitution of metallammonium compounds generally, see Werner, *Zeitschrift für Anorganische Chemie*, 1893, vol. iii.

‡ These names denote the characteristic colours of the salts, thus—*prasimus*, leek-green; *fuscus*, swarthy; *crocus*, yellow, &c.

(γ.) *Croceo Salts.*—General formula, $Co_2(NH_3)_8(NO_2)_4{\cdot}R_2$.

Examples
Croceo-cobaltic chloride, $Co_2(NH_3)_8(NO_2)_4{\cdot}Cl_2$.
Croceo-cobaltic sulphate, $Co_2(NH_3)_8(NO_2)_4{\cdot}SO_4$.

III. *Decammonio Salts*—

(a.) *Roseo Salts.*—General formula, $Co_2(NH_3)_{10}(H_2O)_2R_6$.

Examples
Roseo-cobaltic chloride, $Co_2(NH_3)_{10}(H_2O)_2Cl_6$.
Roseo-cobaltic sulphate, $Co_2(NH_3)_{10}(H_2O)_2{\cdot}(SO_4)_3$, $3H_2O$.

(β.) *Purpureo Salts.*—General formula, $Co_2(NH_3)_{10}X_2R_4$ (where X and R are either the same or different acid radicals).

Examples
Chloro-purpureo-cobaltic chloride, $Co_2(NH_3)_{10}Cl_2{\cdot}Cl_4$.
Chloro-purpureo-cobaltic sulphate, $Co_2(NH_3)_{10}Cl_2{\cdot}(SO_4)_2$.
Bromo-purpureo-cobaltic nitrate, $Co_2(NH_3)_{10}Br_2{\cdot}(NO_3)_4$.

(γ.) *Xantho Salts.*—General formula, $Co_2(NH_3)_{10}(NO_2)_2{\cdot}R_4$.

Examples
Xantho-cobaltic chloride, $Co_2(NH_3)_{10}(NO_2)_2{\cdot}Cl_4$.
Xantho-cobaltic bromo-nitrate, $Co_2(NH_3)_{10}(NO_2)_2{\cdot}Br_2{\cdot}(NO_3)_2$.

IV. *Oxy-decammonio Salts.*—General formula, $Co_2(NH_3)_{10}R_4{\cdot}X{\cdot}O(HO)$ (where X is either (HO) or an acid radical either the same as, or different from, R).

Examples
Oxy-decammonio cobaltic chloride, $Co_2(NH_3)_{10}Cl_4{\cdot}(HO){\cdot}O{\cdot}(HO)$.
Anhydro-oxy-decammonio cobalt chloride, $Co_2(NH_3)_{10}Cl_4{\cdot}Cl_2{\cdot}O{\cdot}(HO)$.

V. *Dodecammonio Salts* (luteo-cobaltic salts).—General formula, $Co_2(HN_3)_{12}R_6$.

Examples
Luteo-cobaltic chloride, $Co_2(NH_3)_{12}Cl_6$.
Luteo-cobaltic sulphate, $Co_2(NH_3)_{12}(SO_4)_3$,$5H_2O$.

When cobalt compounds are fused with borax, a clear blue vitreous mass is obtained, which contains a borate of cobalt. A similar blue colour is imparted to ordinary potash glass when a small quantity of a cobalt salt is added to the molten material, owing to the formation of a silicate of cobalt. Under the name of *smalt*, this substance has been manufactured for use as a pigment, by fusing the roasted cobalt ore with quartz sand and pearl-ash. The fused mass of deep blue glass is then finely ground beneath water.

NICKEL.

Symbol, Ni. Atomic weight = 58.7.

Occurrence.—Nickel occurs chiefly in combination with arsenic as *kupfer nickel*,[*] Ni_2As_2; *white nickel*, $NiAs_2$; *nickel glance*, $Ni_2(AsS)_2$, also as *nickel blende*, NiS. Nickel ore almost invariably contains cobalt, and frequently antimony and bismuth.

Modes of Formation.—Nickel is obtained by reducing the oxide with carbon at a high temperature. It may be obtained as a black powder by reducing nickelous oxide in a stream of hydrogen, or by heating nickelous oxalate out of contact with air. It is also obtained as a lustrous coherent deposit by the electrolysis of an ammoniacal solution of the double sulphate of nickel and ammonia.

Nickel in a high state of purity is now being made on a commercial scale by what is known as the "Mond's" process. This consists in passing carbon monoxide over gently heated nickel oxide, whereby the nickel is first reduced and is then taken up by the carbon monoxide to form nickel carbonyl, $Ni(CO)_4$ (see p. 299). This volatile compound is then passed through tubes which are more strongly heated, which causes the compound to decompose into carbon monoxide (which can be again utilised) and metallic nickel. In this way the metal is deposited in the form of a coherent solid, entirely free from cobalt, with which nickel is always associated in its ores.

Properties.—Nickel is a lustrous white metal, with a faint yellow tinge when compared with silver. It is ductile and malleable, and at the same time very hard and tenacious. It is susceptible of a very high polish. Nickel is attracted by the magnet, but loses this property when moderately heated. When obtained by reduction with charcoal, the metal contains a certain amount of carbon (like cast iron), which renders it less malleable, and when produced by reduction of the oxalate at a low temperature the powder is pyrophoric.

In the massive form, nickel is unacted upon by moderately dry air, but in moist air it tarnishes, and becomes covered with a film

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[*] *Kupfer nickel* signifies *the false copper*, and was applied by the Germans in the Middle Ages to this ore, which resembled a copper ore, because they tried in vain to extract copper from it. It is probable that this ore had been smelted along with copper ores, under the belief that it contained copper, by the early ancients. Thus, a coin, 235 B.C., has been found to contain 20 per cent. of nickel.

of nickelous oxide. It decomposes steam only slowly at a red heat, and is slowly attacked by dilute hydrochloric or sulphuric acid (contrast iron).

Nickel is largely used for electro-plating iron and steel articles. It is also employed on an extensive scale in the production of nickel steel for modern armour plate, in which the proportion of nickel reaches 20 or even 30 per cent.

Nickel Alloys.—With copper, and with copper and zinc, nickel furnishes several important alloys. The small coinage in use in Belgium, Germany, and the United States consists of 1 part of nickel and 3 parts of copper; while the so-called *German silver*, or *nickel-silver*, contains in addition about 1.5 part of zinc.

Oxides of Nickel.—Three oxides of nickel have been obtained, namely, nickelous oxide, NiO; nickelic oxide, Ni_2O_3; and nickelo-nickelic oxide, Ni_3O_4. The first alone is basic.

Nickelous Oxide (*nickel monoxide*), NiO, is obtained as a greenish powder by heating nickel carbonate or hydroxide out of contact with air. It is dissolved by acids yielding nickel salts. When heated in hydrogen or carbon monoxide it is readily reduced to the metallic state.

Nickelous Hydroxide, $Ni(HO)_2$, is obtained in a pale green precipitate when potassium hydroxide is added to a solution of a nickel salt; the precipitate has the composition $4Ni(HO)_2,H_2O$. When strongly heated it is converted into nickelous oxide and water. It is readily soluble in acids, forming the nickel salts, and it also dissolves in ammonia and in solutions of ammonium salts.

Nickel Sesquioxide, Ni_2O_3, is obtained as a black powder when the nitrate is decomposed by heat at the lowest temperature. With hydrochloric acid and sulphuric acid it behaves like a peroxide, yielding nickel salts, with the elimination of chlorine and oxygen respectively—

$$Ni_2O_3+6HCl = 2NiCl_2+3H_2O+Cl_2.$$
$$Ni_2O_3+2H_2SO_4=2NiSO_4+2H_2O+O.$$

It is soluble in ammonia, with evolution of nitrogen—

$$2Ni_2O_3+2NH_3=6Ni(HO)_2+3H_2O+N_2.$$

Hydrated Sesquioxide of Nickel, $Ni_2(HO_6)$, or $Ni_2O_3,3H_2O$. When chlorine is passed through water or sodium hydroxide, in which nickelous hydroxide, $Ni(HO)_2$, is suspended, a black powder is obtained having the composition $Ni_2O_3,3H_2O$. The same compound is obtained when a nickel salt is added to a solution of bleaching-powder. In contact with acids and ammonia it behaves like the oxide.

Nickelo-nickelic Oxide, Ni_3O_4, is obtained as a grey metallic-looking mass, when nickel chloride is heated to about 400° in a stream of oxygen.

Nickel Salts.—Nickel forms only one series of salts, corresponding to the monoxide. In the anhydrous state these are usually yellowish, while in the hydrated condition they are green.

Nickel Chloride, $NiCl_2$, is obtained as a yellow amorphous mass, by dissolving the oxide or carbonate in hydrochloric acid, and evaporating the solution to dryness. When heated in a current of chlorine it sublimes in the form of lustrous golden yellow scales, which dissolve in water, forming a green solution. From the aqueous solution, green crystals of the composition $NiCl_2,6H_2O$ are deposited.

Anhydrous nickel chloride absorbs gaseous ammonia, forming the compound $NiCl_2,6NH_3$, which when deposited from an aqueous solution forms blue octahedrons.

Nickel Sulphate, $NiSO_4,7H_2O$, is produced when the metal, the carbonate, or the oxide is dissolved in dilute sulphuric acid, and the concentrated solution is allowed to crystallise at the ordinary temperature. It forms green crystals, isomorphous with magnesium sulphate. When heated to 100° the crystals lose $6H_2O$, and above 300° the salt becomes anhydrous. The anhydrous salt absorbs gaseous ammonia, being converted into a pale violet powder having the composition $NiSO_4,6NH_3$. When nickel sulphate is dissolved in strong aqueous ammonia, the solution deposits dark blue tetragonal crystals of $NiSO_4,4NH_3,2H_2O$.

With sulphates of the alkalies, nickel sulphate forms double salts, of which the ammonium salt is the most important, $NiSO_4,(NH_4)_2SO_4,6H_2O$. It is obtained by mixing concentrated solutions of the two sulphates in the requisite proportions. This salt is employed in the process of nickel-plating.

Nickelous Sulphide (*nickel monosulphide*), NiS, occurs as the mineral *capillary pyrites*. It is obtained as a bronze-like mass, insoluble in hydrochloric acid, by heating sulphur and nickel together. In the hydrated condition nickel sulphide is precipitated as an amorphous black powder, on the addition of ammonium sulphide to a nickel salt. The precipitate is scarcely soluble in hydrochloric acid, but partially dissolves in excess of ammonium sulphide, forming a brown solution. Three other sulphides have been obtained, having the composition Ni_2S, NiS_2, and Ni_3S_4.

CHAPTER XIV

THE TRANSITIONAL ELEMENTS OF THE SECOND AND FOURTH LONG PERIOD

Ruthenium, Ru=101.7. ***Rhodium***, Rh=103. Palladium, 106.
Osmium, Os=191. Iridium, Ir=193. Platinum, 194.8.

THESE elements, although constituting *two* transitional groups, are very closely related to each other. In nature they all occur associated together in what is commonly known as ***platinum ore***, and they are on this account usually spoken of as ***the platinum metals.***

Platinum ore, or ***native platinum***, contains all these elements in the metallic state. It is found in small grains, sometimes in nuggets, in alluvial deposits and river sand, principally in Brazil, Borneo, California, Australia, and the Urals. Native platinum contains from 60 to 86 per cent. of platinum, the remainder consisting of the other five metals of the group, together with varying quantities of gold, copper, and iron. Amongst the grains of platinum ore there are also found grains which consist essentially of an alloy of platinum and iridium (containing from 30 to 75 per cent. of iridium) known as ***platin-iridium:*** and also particles of an alloy of osmium and iridium (called ***osmiridium***), which contain from 30 to 40 per cent. of osmium, as well as small quantities of rhodium and ruthenium.

They are all white lustrous metals, having high melting-points. They are unacted upon by air or oxygen at ordinary temperatures; and, with the exception of osmium (which burns when strongly heated, forming the tetroxide), they are scarcely oxidised by oxygen at any temperature.

With the exception of palladium, which readily dissolves in hot nitric acid, these metals are unacted upon by ordinary acids. *Aqua regia* converts osmium into the tetroxide; it dissolves platinum with formation of the tetrachloride, and slowly acts upon ruthenium, but is without action upon rhodium and iridium.

The specific gravities of the metals of the first group, although very close to one another, are widely different from those of the second group; and it will be seen that the specific gravities fall, with increasing atomic weights, thus—

Ru, sp. gr.=12.26. Rh, sp. gr.=12.1. Pd, sp. gr.=11.4.
Os, ,, =22.47. Ir, ,, =22.38. Pt, ,, =21.5.

The element osmium is the heaviest known substance.

The most easily fusible of these metals is palladium, which melts about the temperature of wrought iron. The melting-point of platinum is somewhat higher, but it may be boiled by the oxyhydrogen flame. Rhodium and iridium come next in order of fusibility, the latter metal being just fusible by the oxyhydrogen flame, while ruthenium has a still higher melting-point. Osmium has not been melted. When heated to the melting-point of iridium, osmium volatilises; and if air be present, it burns.

The following oxides of these metals are known—

—	—	—	—	Pd_2O	—
RuO	OsO	RhO	—	PdO	PtO
Ru_2O_3	Os_2O_3	Rh_2O_3	Ir_2O_3	—	—
RuO_2	OsO_2	RhO_2	IrO_2	PdO_2	PtO_2
RuO_4	OsO_4	—	—	—	—

Ruthenium, osmium, rhodium, and iridium form salts corresponding to the sesquioxide, such as ruthenious chloride, Ru_2Cl_6; rhodium sulphate, $Rh_2(SO_4)_3$; iridious chloride, Ir_2Cl_6.

With the exception of rhodium, they all form chlorides, corresponding to the dioxides, thus—ruthenic chloride, $RuCl_4$; iridic chloride, $IrCl_4$; platinic chloride, $PtCl_4$, while palladium and platinum yield pallad*ous* and platin*ous* compounds, corresponding to their monoxides.

The tetroxides of ruthenium and osmium are remarkable in melting at an extremely low temperature (about 40°), and boiling about 100°. They yield intensely irritating vapours, which, in the case of osmium tetroxide, exerts a most injurious effect upon the eyes, and is extremely poisonous. (Osmium tetroxide is commonly known as *osmic acid.*) Osmium and ruthenium also exhibit a non-metallic character in forming compounds derived from the unknown ruthenic and osmic trioxides, such as potassium ruthenate, K_2RuO_4, and potassium osmate, K_2OsO_4 (the corresponding ruthenic and osmic acids are unknown). Ruthenium also forms potassium per-ruthenate, $KRuO_4$ (analogous to permanganate), although the corresponding acid and peroxide, Ru_2O_7, are unknown. The most important of these elements is platinum.

PLATINUM.

Symbol, Pt. Atomic weight = 194.8.

In order to separate platinum from the other metals with which the *native platinum* (see page 690) is mixed, the ore is digested in dilute *aqua regia*, under slightly increased pressure. The solution so obtained contains the higher chlorides of platinum, palladium, rhodium, and iridium (for although in the pure state the last two named metals are scarcely attacked by *aqua regia*, when alloyed with much platinum they dissolve). The solution is evaporated to dryness, and heated to 125°, whereby the palladium and rhodium are obtained in the form of their lower chlorides, $PdCl_2$ and Rh_2Cl_6 (the latter of which, in the anhydrous condition, is insoluble in water). The residue is extracted with water, and to the clear solution, acidified with hydrochloric acid, ammonium chloride is added. The double chloride of platinum and ammonium ($PtCl_4,2NH_4Cl$), separates out as yellow crystals, while the corresponding iridium salt, being more soluble, remains for the most part in solution, and may be obtained by concentrating the mother-liquor. The ammonium platinic chloride, on being ignited, loses ammonium chloride and chlorine, leaving the metal in the form of a black spongy mass known as *spongy platinum*, which is then melted by means of the oxyhydrogen flame in a lime crucible. The platinum so obtained usually contains small quantities of iridium and traces of associated metals.

Pure platinum is obtained by alloying commercial platinum with pure le[illegible], and treating the alloy first with nitric acid, which dissolves any copper and iron, a part of the palladium and rhodium, and most of the lead; and then with dilute *aqua regia*, which dissolves the whole of the platinum and the remaining lead, with traces of rhodium. From this solution the lead is precipitated as sulphate, and the platinum is then precipitated as the double chloride, by ammonium chloride. To remove traces of rhodium which are present, the dried double chloride is ignited with hydrogen potassium sulphate, whereby the rhodium is converted into a soluble double sulphate of rhodium and potassium, while the platinum is reduced to the condition of the spongy metal.

Properties.—Platinum is a lustrous, greyish-white, malleable, and ductile metal. At a red heat it may be welded with great ease. It is melted by the oxyhydrogen flame, and vessels of platinum are readily made by fusing the metal together in this way. Heated platinum absorbs large quantities of hydrogen (see page 179); and when the metal is melted in the oxyhydrogen flame, it exhibits the phenomenon of "spitting," when it again solidifies (see Silver, page 562). Platinum does not combine with oxygen at any temperature, neither does the heated metal absorb this gas; but it has the property, when cold, of condensing oxygen upon its surface. A piece of clean platinum foil or wire, when introduced into a mixture of oxygen, and a readily inflammable gas or vapour (such as hydrogen, ether, alcohol, &c.), causes their combination; and occasionally the metal becomes red hot, and ignites the mixture. This action is more rapid in the case of platinum sponge, when a larger surface is brought into play, and a fragment of this material introduced into a detonating mixture of oxygen and hydrogen at once determines its explosion.

Platinum is not acted upon by either nitric or hydrochloric acid. It is oxidised when fused with caustic alkalies, or with potassium nitrate, and is also attacked by fused alkaline cyanides. In the form of sponge, it is dissolved by boiling potassium cyanide, with the evolution of hydrogen and formation of a double cyanide.

Platinum readily combines with phosphorus, silicon, and carbon. The carbide of platinum is formed when the metal is continuously heated by a smoky flame, or one in which combustion is incomplete, hence care is necessary in the use of platinum vessels.

Platinum Black is the name given to the finely-divided metal obtained by precipitating platinum from its solutions by reducing agents or by metals. It is a soft, black powder, which is capable of absorbing, or condensing upon its surface, large quantities of oxygen. It therefore acts as a powerful oxidising agent.

Platinum Alloys.—Platinum readily alloys with many metals; hence compounds of easily reducible metals should not be heated in vessels of platinum. The most important alloys are those with iridium. The addition of 2 per cent of iridium is found greatly to increase the hardness and raise the melting-point of platinum. An alloy containing 10 per cent. of iridium resists the corrosive action of chemical reagents to a greater extent than pure platinum (see Fluorine, page 348).

Oxides of Platinum.—Platinous oxide, PtO, and platinic oxide, PtO_2, are obtained in the form of dark grey or black powders by gently heating the corresponding hydroxides. When strongly heated they are converted into the metal.

Platinous Hydroxide, $Pt(HO)_2$, is obtained by the action of potassium hydroxide upon platinum dichloride. It is a black powder, which dissolves in the halogen acids, yielding platin*ous* compounds.

Platinic Hydroxide, $Pt(HO)_4$, is prepared by adding boiling potassium hydroxide to a solution of platinum tetrachloride, and treating the precipitate with acetic acid to remove the potash. When dried it forms a yellowish powder, which is soluble in acids to form platinic salts. Platinic hydroxide behaves both as a weak base and a feeble acid. With stronger bases it forms compounds known as *platinates*, which are yellow crystalline salts. The sodium salt has the composition $Na_2O,3PtO_2,6H_2O$.

Platinum Dichloride (*platinous chloride*), $PtCl_2$, is produced when platinum tetrachloride is heated to about 250°. It forms a greenish powder, insoluble in water. It dissolves in hydrochloric acid, giving a reddish-brown solution which is believed to contain the double compound $PtCl_2,2HCl$, or H_2PtCl_4, to which the name *chloro-platinous acid* has been given. The compound has never been isolated, but a number of double salts of platinous chloride with other chlorides are known, which may be regarded as derivatives of this acid, and which are therefore termed chloro-platinites; thus, potassium platinous chloride, $2KCl,PtCl_2$, or potassium chloro-platinite, K_2PtCl_4, is obtained as fine red crystals, by adding potassium chloride to a solution of platinous chloride in hydrochloric acid. This salt is used in the *platinotype* photographic process.

Platinum Tetrachloride (*platinic chloride*), $PtCl_4$, is obtained by dissolving the metal in *aqua regia*, and removing the excess of the acids by evaporating to dryness and gently heating the residue. From its aqueous solution, the salt deposits in large red crystals having the composition $PtCl_4,5H_2O$, which are not deliquescent. When the salt is crystallised from a hydrochloric acid solution, or when the *aqua regia* solution is evaporated to expel the nitric acid, with frequent addition of hydrochloric acid, the double compound of platinic chloride and hydrochloric acid is formed, $PtCl_4,2HCl$, which is deposited as reddish-brown deliquescent crystals, with $6H_2O$. To this substance (which is commonly called platinic chloride), the name *chloro-platinic acid* has been given, and the double salts of platinic chloride and various chlorides are regarded as salts of this acid. The most important of these chloro-platinates are those of the alkali metals, their different solubilities being made the basis for the separation of these metals.

Potassium Chloro-platinate (or *potassium platinic chloride*), $2KCl,PtCl_4$ or K_2PtCl_6, is obtained as a yellow crystalline precipitate by adding potassium chloride to platinic chloride. It is soluble in 100 parts of water at the ordinary temperature to the extent of 1.1 part, and at 100°, 5.18 parts. It is insoluble in alcohol.

The rubidium and caesium compounds are very similar, but are still less soluble in water, 100 parts of water at 20° dissolving 0.141 of the rubidium and 0.07 of the caesium salt.

Ammonium Chloro-platinate, $2NH_4Cl,PtCl_4$, closely resembles the potassium salt, being slightly less soluble, but more so than the rubidium compound.

Sodium Chloro-platinate, $2NaCl,PtCl_4,6H_2O$, is a reddish-yellow salt, readily soluble in both water and alcohol.

Platino-cyanides.—Just as platinous chloride combines with metallic chlorides to form chloro-platinites, so platinous cyanide, $Pt(CN)_2$, unites with other cyanides, forming similarly constituted double compounds, known as platino-cyanides.*

Potassium platino-cyanide, $K_2Pt(CN)_4$, or $2KCN,Pt(CN)_2$, is formed when spongy platinum is dissolved in boiling potassium cyanide. The platino-cyanides may be regarded as the salts of platino-cyanic acid, $H_2Pt(CN)_4$. Both the acid and the salts are characterised by the wonderful play of colours they exhibit when viewed in different lights, and by forming different coloured crystals with varying quantities of water of crystallisation (see page 217).

Sulphides of Platinum.—Platinous sulphide, PtS, and platinic sulphide, PtS_2, are obtained as amorphous black powders by the action of sulphuretted hydrogen upon the respective chlorides.

Oxysalts of Platinum.—Few well-defined single salts of platinum with oxyacids are known. This element, however, exhibits a great tendency to form complex double salts. One such series of compounds is seen in the *platino-nitrites*, which may be regarded as the salts of platino-nitrous acid, $H_2Pt(NO_2)_4$.

These salts are remarkable, in that the platinum they contain cannot be detected by the ordinary tests for that metal; just as the iron present in ferro-cyanides is not detected by the ordinary reagents used in testing for that metal.

Ammoniacal Platinum Bases, or **Platinamines.**

Like cobalt, platinum forms a large number of basic compounds with ammonia, many of which are of extremely complex composition. The first of these to be discovered was a bright green salt, obtained by the action of ammonia upon platinous chloride, having the composition $PtCl_2,2NH_3$, or $Pt(NH_3)_2Cl_2$, and known as *the green salt of Magnus.* Many of the platinamines exhibit isomerism; thus, a compound known as the *chloride of Reiset's second base* is a yellow crystalline salt having the same composition as Magnus's green salt. Twelve distinct series of ammoniacal platinum compounds are known, four of which are derived from platin*ous* and the remainder from platin*ic* salts; the former are termed *platoso* ammonium compounds, while the latter are distinguished as the *platino* compounds.†

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* The name Cyano-platinites might with advantage be applied to these compounds.

† For detailed descriptions of these compounds, the student is referred to larger works on chemistry; and on the constitution of these, and metallammonium compounds generally, the article by Werner, in the *Zeitschrift für Anorganische Chemie*, 1893, vol. iii. p. 267, may be consulted.